Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.fw001

Industrial and Laboratory Nitrations

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.fw001

Industrial and Laboratory Nitrations

Lyle F. Albright, EDITOR
Purdue University

Carl Hanson, EDITOR
University of Bradford, England

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.fw001

A symposium sponsored by
the Division of Industrial
and Engineering Chemistry
at the 169th Meeting of the
American Chemical Society,
Philadelphia, Pa.,
April 7–8, 1975.

ACS SYMPOSIUM SERIES **22**

AMERICAN CHEMICAL SOCIETY

WASHINGTON, D. C. 1976

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.fw001

Library of Congress CIP Data

Industrial and laboratory nitrations.
(ACS symposium series; 22 ISSN 0097-6156)
Papers presented at a symposium held in Philadelphia, Apr. 7 and 8, 1975, as part of the 169th annual meeting of the American Chemical Society, under the sponsorship of the Division of Industrial and Engineering Chemistry.

Includes bibliographical references and index.

1. Nitration—Congresses. I. Albright, Lyle Frederick, 1921- . II. Hanson, Carl. III. American Chemical Society. Division of Industrial and Engineering Chemistry. IV. Series: American Chemical Society. ACS symposium series; 22.

TP156.N5152 660.2′844′6 75-38712
ISBN 0-8412-0306-7 ACS MC8 22-1-357(1975)

Copyright © 1975
American Chemical Society
All Rights Reserved

PRINTED IN THE UNITED STATES OF AMERICA

ACS Symposium Series

Robert F. Gould, *Series Editor*

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.fw001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.fw001

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the SERIES parallels that of its predecessor, ADVANCES IN CHEMISTRY SERIES, except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS SYMPOSIUM SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.pr001

PREFACE

This book contains the full manuscripts of the 23 papers presented during the symposium "Advances in Industrial and Laboratory Nitrations" held in Philadelphia on April 7 and 8, 1975, as part of the 169th Annual Meeting of the American Chemical Society, under the sponsorship of the Division of Industrial and Engineering Chemistry. The Editors had the honor of acting as cochairmen of the symposium. Publication of the proceedings will make the papers available to an even wider audience than the large and international one present in Philadelphia.

Why should a meeting on industrial nitration chemistry have been timely? Nitration, particularly of aromatic hydrocarbons, was one of the earliest unit processes to be operated on a large scale when the heavy organic chemical industry first developed last century. It has played an equally important part in the development of our present understanding of the mechanism of organic reactions, offering an ideal example of electrophilic substitution and being most elegantly researched during the 1940's and 1950's in the classic investigations of Professor C. K. Ingold and his associates at University College, London (J. Chem. Soc. (Brit.) 1950, 2400-2473; 1950, 2628-2684; 1952, 28-32; and 1958, 4357-4374). Despite a long history of industrial application and the extensive study of nitration mechanisms, many questions remain to be answered, and the last decade has seen a resurgence of interest in the chemistry of the process, particularly under the conditions employed in industry.

Having worked together for a considerable number of years, we came to the conclusion that the time was ripe on both sides of the Atlantic Ocean for a major international meeting aimed at reviewing our present state of knowledge and at convening the chemists and chemical engineers, from both industrial and academic establishments, who have been working on the subject. The Philadelphia symposium was the result. We were particularly concerned about providing a medium for interaction among all scientists—of whatever discipline or employment—who had something to offer toward a better understanding of nitration reactions under industrial conditions. There have been previous meetings on nitrations, but we feel this to be the first at which such a wide spectrum of sources was sought and obtained.

The first group of papers, Chapters 1–10 of this book, emphasize various aspects of the chemistry and the mechanism of different nitrations. Information on side reactions, including oxidation, and on *ipso* nitrations is discussed by several authors; such information should be most helpful in clarifying certain features of the overall process. During the symposium, the results of Ingold and associates were referred to on numerous occasions; they had clearly shown that the nitronium ion, NO_2^+, is an excellent nitrating agent. They also indicated the nitrosonium ion, NO^+, can be used in the nitration of easily nitratable aromatics including phenols or phenol ethers. Other ions which result in nitrations have also now been reported in Chapter 1.

The second broad grouping of papers (Chapters 11–16) considers both the chemistry and physical transfer steps between phases which often occur during nitration. In aromatic nitrations using mixed acids, for example, the presence of two immiscible liquid phases complicates the nitration reaction. Agitation to emulsify the two phases is necessary to obtain adequate contact between the hydrocarbon and the nitrating species. Transfer of reactants and products, heat transfer, nature of emulsion, etc. are key factors.

Chapters 17–24 consider various aspects of plant operation. Process improvements, safety features, and new processes are discussed; in several cases nitration chemistry is also presented.

The present volume contains two papers in addition to those formally presented at the symposium. The first (Chapter 24) concerns development of an industrial nitration plant employing injectors for mixing the liquid streams. While an offer of this paper was received prior to the symposium, there was insufficient notice for it to be incorporated into the program. Nevertheless, we feel it to be of interest and direct relevance to the symposium and so have included it for the benefit of the reader. The second paper (Chapter 25) is devoted to vapor phase nitrations and was presented at an earlier American Chemical Society meeting. Since the papers presented at the symposium were concerned primarily with liquid phase processes, we thought that, because of their industrial importance, vapor phase nitrations should be included also.

In conclusion, we would like to thank all who made possible the symposium and this subsequent publication: firstly, the Division of Industrial and Engineering Chemistry for sponsorship; equally important, the authors, without whom it could never have existed; and finally, those who have worked behind the scenes, particularly our two secretaries, Mrs. Diane Kneile (West Lafayette) and Mrs. P. A. Matthews (Bradford), who have been burdened with considerably more than their normal duties as a result.

Lyle F. Albright
West Lafayette, Ind. USA
October 1975

Carl Hanson
Bradford
England

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.pr001

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Preparative and Mechanistic Aspects of Electrophilic Nitration

GEORGE A. OLAH

Case Western Reserve University, Cleveland, Ohio 44106

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Electrophilic nitration of aromatics is the most studied, and supposedly best understood of organic reactions (1). Culminating their work, Ingold, Hughes, and their associates in 1950 published simultaneously a series of papers (2) which rightfully ever since is considered the most fundamental study in our understanding of electrophilic nitration reactions. Thus, not unexpectedly, for years following these publications the general view prevailed, that all the significant work in nitration was done, and little additional knowledge was to be gained. Chemists' interest consequently rapidly faded in the field, and by the end of the 1950's from a scientific point of view the study of nitration looked like as one of the most unattractive and inactive areas. In a way, no greater compliment of the achievements of Ingold and his group could have been made than the generally accepted view, that their work indeed, completed what there was worthwhile to study in nitration. Any further research, indeed, seemed to be directed only to fill in the few still uncompleted details for reviews in text books and scientific monographs.

In 1975, a quarter of a century after the appearance of the Ingold papers, the field of electrophilic nitration, as testified by this broad scope symposium,is again a field of substantial interest and activity. This is the case both as far as the more practical, preparative and technical aspects of nitration are concerned, and equally so concerning the mechanistic and basic aspects of the field. It is, of course, an old cliché to say that each generation of chemists feels that their work is the last word in their field, and nothing new ever will be added. I for one, however, strongly feel that chemistry is certainly not a closed-end chapter, and we are just starting to realize and explore in many areas how limited our knowledge still is. The renewed interest in nitration clearly testifies to this point. With my group, we have had the good fortune to be able to contribute something in the last two decases to rekindle interest in nitration reactions. It is thus a great pleasure and privilege to be

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

able at this Symposium to briefly summarize some of our own research and its more recent aspects, as well as to try at the end of my lecture to indicate some of the areas where I think continued work would promise significant new advances and results. It certainly would be most fascinating to foresee what a future symposium on nitration would present in another quarter of a century, heralding in the new millennium. But, many of us may not be around any more for the occasion. However, maybe some of the younger generation will look up at the time the published volume of this Meeting, and glancing over what we were interested in, studying and projecting, compare it with the obviously vastly more fundamental knowledge acquired by the year 2000. For the record then let's try to give you a brief account of what I have to present in 1975 with some comparison of where our knowledge stood in 1950. I hope that the symposium of 2000 will look back at our present limited efforts with some degree of acknowledgment and conclude that our present generation contributed to the continued progress of a clearly fascinating and very practical field.

Preparative Aspects

Nitration with Nitronium Salts (Olah-Kuhn Nitration). The Ingold group (2) clarified the nature of the salt obtained by Hantsch (3) from nitric and perchloric acids as a mixture of nitronium perchlorate, and hydronium perchlorate. They subsequently prepared, and studied (by Raman spectroscopy) pure nitronium perchlorate (2). This was a significant step, because even if in a separate system, but it directly proved the existence of the nitronium ion suggested by their kinetic studies. Nitronium perchlorate, however, has received little subsequent interest. I once was told by the late Professor Ingold that he had a small sample of the compound in a sealed vial on his desk which one morning shattered. This was very much the end of interest at University College in what was considered an unstable, dangerous compound.

My own research work on electrophilic nitration, which started in Hungary in the early 1950's, showed, however, that any difficulty connected with nitronium perchlorate was not at all the fault of the cation, but of the rather unsuitable perchlorate anion. As it is well recognized now, perchlorate salts generally are rather unstable and susceptible to explosive behavior because of their ability to form covalent esters. In the case of nitronium perchlorate the isolated crystalline nitronium salt can form, in equilibrium, small amounts of the covalent nitryl perchlorate ester which then could be susceptible to explosive decomposition.

$$NO_2OClO_3 \rightleftharpoons NO_2^+ClO_4^-$$

To prepare nitronium salts as stable nitrating reagents thus necessitated the use of counter ions, which could give no unstable esters. We reported in 1956 with Steve Kuhn the simple preparation of nitronium tetrafluoroborate, and its application as a nitrating agent (4,5).

Nitronium tetrafluoroborate is most conveniently prepared by adding anhydrous HF to nitric acid in a solvent such as nitromethane, methylene chloride etc, and then saturating the solution with BF_3

$$HNO_3 + HF + 2BF_3 = NO_2^+BF_4^- + BF_3 \cdot H_2O$$

A nearly quantitive yield of the stable nitronium salt can be obtained. An undergraduate in an afternoon's work, can prepare up to a pound of the salt which is now also commercially available. To my best knowledge in its two decades of use, there was never any difficulty connected with its stability. Nitronium tetrafluoroborate, and subsequently other complex fluoride salts, such as the hexafluorophosphate, have gained widespread application as most reactive nitrating agents.

Nitronium salts are colorless, crystalline, very stable compounds; $NO_2^+BF_4^-$ decomposes at atmospheric pressure only above 170°, without subliming, into its components: $NO_2F + BF_3$. The hexafluoroantimonate salts are even more stable. The higher thermal stability may be partially also a consequence of the higher boiling points of the corresponding Lewis acid fluorides compared to boron trifluoride.

Nitronium salts can be stored at room temperature indefinitely without decomposition. Refrigeration is unnecessary and no other special precautions are required. All nitronium salts are, however, very hygroscopic and must be stored and handled with precautions to avoid moisture.

Nitronium tetrafluoroborate and related nitronium salts are extremely active nitrating agents for aromatics

$$ArH + NO_2^+BF_4^- \longrightarrow ArNO_2 + HF + BF_3$$

The nitrations are carried out under anhydrous conditions. This is of special advantage in dealing with compounds which under usual strong acidic nitration conditions may undergo hydrolysis or oxidation. Aryl nitriles, for example, are easily hydrolyzed under nitration conditions and no direct dinitration, requiring forceful conditions, was previously possible. The nitronium fluoroborate method enable us to carry out mono and dinitration of aryl nitriles with high yields without any hydrolysis of the -CN group.

Results of preparative nitrations of arenes, haloarenes, nitroarenes, arylcarboxylic acid esters and halides and arylnitriles are summarized in Tables I-V.

Generally a three fold excess of the aromatic was nitrated at 20° if not otherwise stated. Yields relate to isolated nitro

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

TABLE I

NITRATION OF ARENES WITH $NO_2^+BF_4^-$ [a]

Substrate	Product	Reaction time, min.	Yield of isolated mononitro product, %
Benzene	Nitrobenzene	10	93
Toluene	Nitrotoluenes	10	95
o-Xylene	Nitroxylenes	10	91
m-Xylene	Nitroxylenes	10	90
p-Xylene	Nitro-*p*-xylene	10	93
Mesitylene	Nitromesitylene	10	89
Ethylbenzene	Nitroethylbenzenes	10	93
n-Propylbenzene	Nitro-*n*-propylbenzenes	10	91
i-Propylbenzene	Nitro-*i*-propylbenzenes	10	93
n-Butylbenzene	Nitro-*n*-butylbenzenes	10	90
sec-Butylbenzene	Nitro-*sec*-butylbenzenes	10	92
t-Butylbenzene	Nitro-*t*-butylbenzenes	10	88
Naphthalene	Nitronaphthalenes	25	79
Anthracene	9-Nitroanthracene	25	85

[a] All nitrations were carried out in tetramethylene sulfone solutions at temperatures between 0 and +5°.

TABLE II

NITRATION OF HALOARENES AND HALOARALKANES WITH $NO_2^+BF_4^-$

Substrate	Product	Reaction temp., °C.	Reaction time, min.	Yield of mononitro prod., %
Fluorobenzene	*o,p*-Fluoronitrobenzenes	5	10	90
Chlorobenzene	*o,p*-Chloronitrobenzenes	10	10	92
Bromobenzene	*o,p*-Bromonitrobenzenes	10	10	87
Iodobenzene	*o,p*-Iodonitrobenzenes	10	10	90
Benzotrifluoride	*m*-Nitrobenzotrifluoride	30	20	20
p-Fluorobenzotrifluoride	3-Nitro-4-fluoro-benzotrifluoride	50	20	85
o-Dichlorobenzene	Nitro-*o*-dichlorobenzenes	50	20	70
m-Dichlorobenzene	Nitro-*m*-dichlorobenzenes	50	20	74
p-Dichlorobenzene	Nitro-*p*-dichlorobenzene	50	20	80
o-Difluorobenzene	Nitro-*o*-difluorobenzenes	50	20	82
m-Difluorobenzene	Nitro-*m*-difluorobenzenes	50	20	79
p-Difluorobenzene	Nitro-*p*-difluorobenzene	50	20	85
α-Fluoronaphthalene	Nitro-α-fluoronaphthalenes	30	20	75
β-Fluoronaphthalene	Nitro-β-fluoronaphthalenes	30	20	79
Benzyl chloride	Nitrobenzyl chlorides	0	10	52
β-Fluoroethylbenzene	Nitro-β-fluoroethylbenzenes	0	10	69
β-Chloroethylbenzene	Nitro-β-chloroethylbenzenes	10	15	82
β-Bromoethylbenzene	Nitro-β-bromoethylbenzenes	10	15	78

TABLE III

NITRATION OF NITROARENES AND NITROHALOARENES WITH $NO_2^+BF_4^-$ [a]

Substrate	Product	Reaction		Yield of nitro prod., %
		Temp., °C.	Time	
Nitrobenzene	*m*-Dinitrobenzene	25	20 min.	81
α-Nitronaphthalene	Dinitronaphthalenes	25	20 min.	85
p-Fluoronitrobenzene	2,4-Dinitrofluorobenzene	30	30 min.	78
o-Fluoronitrobenzene	2,4-Dinitrofluorobenzene	30	30 min.	84
2,4-Dinitrofluorobenzene	Picryl fluoride	120	12 hr.	40
p-Nitrochlorobenzene	2,4-Dinitrochlorobenzene	30	30 hr.	75
o-Nitrochlorobenzene	2,4-Dinitrochlorobenzene	30	20 hr.	77
2,4-Dinitrochlorobenzene	Picryl chloride	100	10 hr.	80

[a] Tetramethylene sulfone was used as the solvent in all cases except for 2,4-dinitrofluoro- and 2,4-dinitrochlorobenzene when 100% H_2SO_4 was used.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

TABLE IV

NITRATION OF ARYLCARBOXYLIC ACID ESTERS AND HALIDES WITH $NO_2^+BF_4^-$ [a]

Substrate	Product	Reaction		Yield of mononitro prod., %
		Temp., °C.	Time, min.	
Methyl benzoate	*m*-Nitromethyl benzoate	30	20	88
Ethyl benzoate	*m*-Nitromethyl benzoate	30	20	79
Propyl benzoate	*m*-Nitropropyl benzoate	30	20	82
m-Nitroethyl benzoate	3,5-Dinitroethyl benzoate	85–90	120	60
Benzoyl fluoride	*m*-Nitrobenzoyl fluoride	50	30	69
Benzoyl chloride	*m*-Nitrobenzoyl chloride[b]	50	30	70

[a] All nitrations were carried out in tetramethylene sulfone solutions. [b] Halogen exchange to acid fluoride takes place with by-product HF.

TABLE V

NITRATION OF ARYL AND ARALKYL NITRILES WITH $XO_2^+BF_4^-$ [a]

Substrate	Product	Reaction		Yield of nitro prod., %
		Temp., °C.	Time, min.	
Benzonitrile	3-Nitrobenzonitrile	20–35	30	85
o-Toluonitrile	2-Methyl-5-nitrobenzonitrile	20–35	30	90
m-Toluonitrile	Nitrotoluonitriles	20–35	30	85
p-Toluonitrile	4-Methyl-3-nitrotoluonitrile	20–35	30	92
Nitro-*o*-toluonitrile	3,5-Dinitro-*o*-toluonitrile	100	60	93
Nitro-*m*-toluonitrile	Dinitro-*m*-toluonitriles	100	60	84
Nitro-*p*-toluonitrile	3,5-Dinitro-*o*-toluonitrile	100	60	89
p-Fluorobenzonitrile	4-Fluoro-3-nitrobenzonitrile	40–50	30	90
p-Chlorobenzonitrile	4-Chloro-3-nitrobenzonitrile	50–55	40	92
1-Naphthonitrile	Nitronaphthonitrile	20–35	30	91
Benzyl cyanide	Nitrobenzyl cyanides	0–15	15	84

[a] All nitrations were carried out in tetramethylene sulfone solutions using a ratio of ArCN:NO_2BF_4 of 1:1.25 in mononitrations and a ratio of $ArNO_2CN$:NO_2BF_4 of 1:2 in dinitrations.

compound in preparative scale nitrations and not to infrared or gas chromatographic analyses. No attempt was made to obtain optimum yields. In the case of mononitrations, which are generally very fast with the exception of highly deactivated substrates, the nitrations are almost quantitative. Di- and trinitrations could also give considerably higher yields then reported, with longer reaction times, higher temperatures or by simply finding more suitable reaction conditions.

Nitronium tetrafluoroborate nitrations were carried out in tetramethylene sulfone solutions. The use of homogeneous, acid free (with the exception of HBF_4 which is formed as by-product in equimolar quantities and is quite stable as the conjugate acid in tetramethylene sulfone solution) reaction media makes it possible to carry out mononitrations, using an excess of the aromatic substrate, with only a limited amount (<3%) of higher nitrated products formed. This is a definite advantage over mixed-acid nitrations where,due to the higher solubility of the mononitro products in the acid layer, dinitrations can be more significant.

Nitronium salts have generally very low solubilities in or-

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

ganic solvents which themselves do not react with $NO_2^+ BF_4^-$. $NO_2^+SbF_6^-$, $NO_2^+PF_6^-$ and $NO_2^+AsF_6^-$ are, however, quite soluble in nitromethane (up to 50% solutions can be prepared at 25°) and, therefore, suited for preparative nitrations. Tetramethylene sulfone is a good solvent for nitronium salts and aromatic substrates alike. The saturated tetramethylene sulfone solution of NO_2BF_4 is about 7% (0.5 molar). Its high dielectric constant ($\varepsilon = 44$) is particularly advantageous and as it is completely miscible with water the separation of products from the nitration mixtures is very easy. The only disadvantage is its relatively high freezing point (+ 28.9°) which is, however, somewhat compensated by its high molar depression (66.2°) which allows to carry out nitrations at reasonably low temperatures when required.

A number of other solvents were also found applicable to a varying degree in nitronium salt nitrations. One of these is acetonitrile. The saturated solution of $NO_2^+BF_4^-$ in acetonitrile at room temperature is about 10% (weight). As acetonitrile is also an excellent solvent for most aromatics and is also miscible with water, it has the same advantages as tetramethylene sulfone. It reacts, however, at higher temperatures and even slowly on standing at room temperature with nitronium salts. Therefore, only fresh solutions can be used and nitrations must be carried out at lower temperatures.

Anhydrous acetic acid was suggested together with methanesulfonic acid as solvents for nitronium tetrafluoroborate nitrations by Giaccio and Marcus (6). Acetic acid, although a good solvent for both nitronium salts and aromatics, does react with nitronium tetrafluoroborate even on standing at room temperature, with the formation of acetyl nitrate. The nitrating power of

$$CH_3COOH + \overset{+}{NO_2}\overset{-}{BF_4} \rightleftharpoons CH_3COONO_2 + HF + BF_3$$

acetyl nitrate is quite different from nitronium tetrafluoroborate, as is its stability. This limits its use as a suitable solvent in preparative nitrations, as well as in kinetic and reaction mechanism investigations. Aromatic hydrocarbons are almost completely insoluble in methanesulfonic acid, thus making homogeneous nitrations possible only in very high dilutions; 100% sulfuric acid could be used successfully in heterogeneous nitrations with $NO_2^+ HS_2O_7^-$ when forceful reaction conditions were required for highly deactivated compounds.

When carrying out mono- or dinitration of aromatics, nitronium salts generally react under quite mild conditions, and yields are 80-100%.

Trinitration of aromatics, particularly benzene represented a challenging problem. Although the preparation of 1,3,5-trinitrobenzene from m-dinitrobenzene has been reported in low yield (7-9), 1,3,5-trinitrobenzene is usually prepared by indirect methods (10). The nitration of m-dinitrobenzene to 1,3,5-trinitrobenzene with nitronium tetrafluoroborate in fluorosulfuric acid

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

solution can be carried out with ease. At temperatures below 100° the nitration is however, too slow to be of preparative use. Only a 40% yield (based on the isolated products) of 1,3,5-trinitrobenzene was observed (11) even after several days. However, the recovery of nitro products was almost quantitative (98.8% based on the starting *m*-dinitrobenzene).

The rate of conversion of *m*-dinitrobenzene to 1,3,5-trinitrobenzene, as expected, increases with increasing reaction temperature. However, the overall recovery of nitro products decreases with increased reaction temperature, due to oxidative side reactions. Thus, it was necessary to carry out a detailed study to find optimal reaction conditions (12,13). The results of these studies at 150° are shown in Table VI. With a reaction time ∿ 2h, one can obtain a 66% yield of 1,3,5-trinitrobenzene. However, since there is unreacted *m*-dinitrobenzene present (about 17%), a separation process (such as high pressure liquid chromatography) is needed in order to obtain pure 1,3,5-trinitrobenzene. A reaction time of 3h gave a ∿ 62% yield of 1,3,5-trinitrobenzene with 95% purity. With 3.8h reaction time, 100% purity was achieved, but the yield dropped to about 50%.

TABLE VI

Nitration of *m*-Dinitrobenzene to 1,3,5-Trinitrobenzene with Nitronium Tetrafluoroborate ($NO_2^+BF_4^-$) in Fluorosulfuric Acid (FSO_3H) Solution at 150

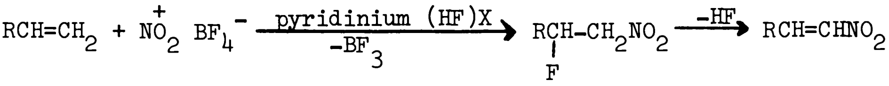
Reaction Time (h)	Recovery of Nitro Compounds[a] (%)	1,3,5-Trinitrobenzene in Total Nitro Products[b] (%)	Yield of 1,3,5-Trinitrobenzene (%)
0	100	0	0
0.5	95.2	38.0	36.2
1.0	90.3	60.4	54.5
1.7	82.5	80.0	66.2
2.2	77.7	85.0	66.0
3.0	64.8	95.0	61.6
3.4	56.7	98.2	55.7
3.6	52.3	99.4	52.0
3.8	49.3	100	49.3
4.0	44.8	100	44.8
4.2	39.4	100	39.4

[a] Based on starting *m*-dinitrobenzene.

[b] Based on total nitro products isolated.

Nitronium salts in strongly acidic solvent (such as FSO_3H or HF) are thus capable to affect an efficient preparative nitration of benzene to 1,3,5-trinitrobenzene, which due to its increased stability over TNT can be of significance.

Aliphatic Nitrations. Nitronium salt nitrations were also extended to nitration of olefinic systems. Nitronium salts readily add to olefins, giving the corresponding nitrofluoroalkanes. This addition is particularly effective when carried out in solvent systems such as pyridinium polyhydrogen fluoride (14).



$$RCH{=}CH_2 + \overset{+}{NO_2}\ BF_4^- \xrightarrow[-BF_3]{\text{pyridinium (HF)X}} \underset{\displaystyle F}{RCH}{-}CH_2NO_2 \xrightarrow{-HF} RCH{=}CHNO_2$$

Dehydrofluorination gives the corresponding nitroolefins. On the other hand, when the olefin is used in excess the nitronium salt can act as a cationic polymerization initiating agent (15).

$$RCH{=}CH_2 + \overset{+}{NO_2} \rightarrow R\overset{+}{C}HCH_2NO_2 \xrightarrow{RCH=CH_2} RC\overset{+}{H}{-}CH_2{-}CHRCH_2NO_2 \xrightarrow{RCH=CH_2} \textbf{Polymer}$$

The polymers formed contain the initiating nitro group.

Perhaps the most fascinating aspect of nitrations with nitronium salts, was the realization that alkanes also undergo with relative ease electrophilic nitrations.

Whereas electrophilic aromatic nitration is one of the most thoroughly studied substitution reactions, electrophilic aliphatic nitration remains virtually unrecognized. Nitration of paraffins was first carried out by Beilstein and Kurbatov in 1880 (16) and subsequently by Konovalov (17) and Markovnikov (18). It was shown that generally higher temperatures and dilute nitric acid is needed to achieve nitration of saturated aliphatic hydrocarbons. Hass (19) in the 1930's developed a practical gas-phase nitration of paraffins like propane, *n*-butane and isobutane, *n*-pentane and isopentane with nitric acid vapor at 350-400°. Grundmann (20) was able to extend the scope of the reaction to higher molecular weight hydrocarbons by carrying out the reaction at 160-180° in the liquid phase, with superheated nitric acid vapor or with nitrogen dioxide. From all these studies it was generally concluded that aliphatic hydrocarbon nitrations are free-radical reactions, with nitrogen dioxide acting as the nitrating agent (21). With Henry Lin, we found (22) that electrophilic nitration and nitrolysis (the terms are defined as substitution of hydrogen for the nitro group and nitrolytic cleavage of C-C bonds), respectively, of alkanes and cycloalkanes with stable nitronium salts can be carried out under well-controlled conditions, excluding the probability of free-radical formation.

A solution of a stable nitronium salt (generally the hexafluorophosphate $NO_2^+PF_6^-$ but also the hexafluoroantimonate $NO_2^+SbF_6^-$ or tetrafluoroborate $NO_2^+BF_4^-$) in solvents such as methylene chloride-tetramethylene sulfone, and the like, is reacted with the alkane (cycloalkane), with usual precautions taken to avoid moisture and other impurities. Reactions were carried out at room temperature (25°) and in the dark in order to avoid or minimize the possibility of radical side reactions and/or protolytic cleavage reactions (tertiary nitroalkanes particularly undergo ready protolytic cleavage reactions). No attempt was made to optimize conditions or increase yields by raising react-

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

ion temperatures. Data obtained are summarized in Table VII.

TABLE VII.

Nitration and Nitrolysis of Alkanes and Cycloalkanes with $NO_2^+PF_6^-$ in CH_2Cl_2–Sulfolane Solution at 25°

Hydrocarbon	Nitroalkane products and their mol ratio
Methane	CH_3NO_2
Ethane	$CH_3NO_2 > CH_3CH_2NO_2$, 2.9:1
Propane	$CH_3NO_2 > CH_3CH_2NO_2 >$ 2-$NO_2C_3H_7 >$ 1-$NO_2C_3H_7$, 2.8:1:0.5:0.1
Isobutane	*tert*-$NO_2C_4H_9 > CH_3NO_2$, 3:1
n-Butane	$CH_3NO_2 > CH_3CH_2NO_2 >$ 2-$NO_2C_4H_9 \sim$ 1-$NO_2C_4H_9$, 5:4:1.5:1
Neopentane	$CH_3NO_2 >$ *tert*-$C_4H_9NO_2$, 3.3:1
Cyclohexane	Nitrocyclohexane
Adamantane	1-Nitroadamantane > 2-nitroadamantane, 17.5:1

Yields of nitro products obtained were, however low (<10%) and by-products are also formed. The effectiveness of nitronium ions in nitration of alkanes can be increased quite substantially when using strongly acidic solvents, such as fluorosulfuric acid (see subsequent discussion of mechanisms). Strongly acidic media, however, cannot be used when the formed nitroalkanes are tertiary, and to a lesser degree secondary. Isobutane for example, in acidic media although initially gives tertiary-nitrobutane subsequently undergoes with great ease cleavage of the tertiary C-N bond. The tertiary butyl cation then deprotonates to isobutylene, giving subsequently complex reaction mixtures. Adamantane is a further interesting example of the study of the nitration of saturated hydrocarbons. Whereas in mixed acid adamantane is very easily oxidized giving adamantanone and complex reaction mixtures, nitronium salts in methylene chloride and related solvents also nitrate adamantane (with a ratio of the 1- and 2- isomers exceeding 10:1). As will be seen in the discussion of the mechanism, this represents a typical electrophilic nitration from the front side, extending the usefulness of electrophilic nitration, and allowing nitration of many bi- and polycyclic hydrocarbons. The draw-back of electrophilic aliphatic nitration at the present time lies in low yield and frequently complex reaction mixtures containing side products arising from cleavage processes. It is, however, clear that alkanes undergo with relative ease electrophilic nitration.

I find it somewhat surprising considering the steadily increasing number of applications, that despite the obvious widespread preparative use of nitronium salts as nitrating agents, generally very little acknowledgment is given to them in this regard. Nitronium salts are generally referred to only relating their application in mechanistic studies of nitration. As much as I myself believe in mechanistic studies, and acknowledge their significance to chemistry, I would like to suggest that in the long run the introduction of nitronium ion salts as preparative

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

reagents into the area of electrophilic nitration will be much more remembered, than some of the interest which surrounds their use in mechanistic studies. Chemistry is and always will be primarily an experimental science. A new, useful general synthetic method or reagent has a more lasting impact than any contemporary emphasis of mechanistic aspects.

Transfer Nitrations with Nitroxonium and - pyridinium Ions

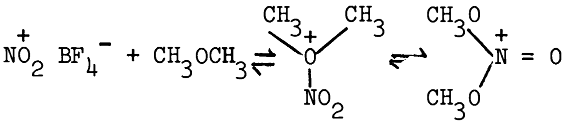
When necessary the selectivity of nitronium salts, such as nitronium tetrafluoroborate in sulfolane, or nitronium hexafluorophosphate in nitromethene can be modified with added complexing agents such as dimethyl ether, dimethyl sulfide, tetrahydrofuran, or methyl alcohol (13,23). The results are shown in Table VIII.

Table VIII clearly shows that the $k_{toluene}/k_{benzene}$ ratios are in the range of 2 to 5, when one equivalent of alcohol, ethers, or thioether is added, while in the range of 25 to 66, when two equivalents is added, and in both cases the relative reactivity of the nitrating agent in the presence of added reagents is in the order of ROH > ROR > RSR. The equilibria in these reactions can be expressed as follows:

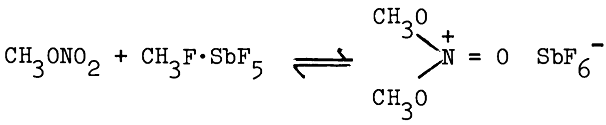
$$NO_2^+PF_6^- + RXR \rightleftharpoons \overset{+}{R}XRNO_2\ PF_6^- \xrightleftharpoons{RXR} RONO_2 + R_3X^+PF_6^-$$

where X is O or S, and R stands for an alkyl group or H.

It is thus indicated that the nitronium ion forms, in equilibrium, the corresponding nitroxonium (nitrosulfonium) ion which can act as selective nitrating agents, or in case of the dimethyl ether complex rearranges to the dimethyl nitracidium ion, which then can act as a nitrating agent or give NO_2^+.



Indeed, in our recent studies (23) we were able to show that the dimethyl nitracidium ion, the dimethyl ether of the nitracidium ion, which is readily prepared by methylating methyl fluoroantimonate can act as transfer nitrating agent, as can N-nitropyridinium salts studied with my wife (24) and also by Cupas and Pearson (25), whose data are summarized in Table IX.



Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

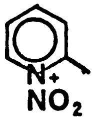
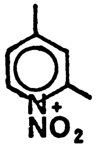
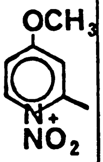
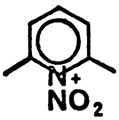
TABLE VIII

COMPETITIVE NITRATION OF BENZENE AND TOLUENE WITH $NO_2^+PF_6^-$ IN THE PRESENCE OF ALCOHOLS, ETHERS, AND THIOETHER IN CH_3NO_2 AT 25°

Nitrating agent	k_T	k_T/k_B	Isomer distribution, %			o/p
			ortho	meta	para	
$NO_2^+PF_6^-$-methanol (1 : 1)		3.31	62.7	3.0	34.3	1.83
$NO_2^+PF_6^-$-methanol (1 : 2)		26.09	62.3	3.2	34.5	1.81
$NO_2^+PF_6^-$-neopentyl alcohol (1 : 1)		2.83	61.7	2.8	35.5	1.74
$NO_2^+PF_6^-$-neopentyl alcohol (1 : 2)		25.40	61.7	3.1	35.2	1.75
$NO_2^+PF_6^-$-methyl ether (1 : 1)		3.96	61.7	3.7	34.6	1.78
$NO_2^+PF_6^-$-methyl ether (1 : 2)		31.33	62.4	3.4	34.2	1.82
$NO_2^+PF_6^-$-ethyl ether (1 : 1)		3.82	62.0	3.7	34.3	1.81
$NC_2^+PF_6^-$-ethyl ether (1 : 2)		32.83	62.5	3.7	33.8	1.85
$NO_2^+PF_6^-$-tetrahydrofuran (1 : 1)		3.56	61.9	3.5	34.6	1.79
$NO_2^+PF_6^-$-tetrahydrofuran (1 : 2)		28.86	62.2	3.6	34.2	1.82
$NO_2^+PF_6^-$-dimethyl sulfide (1 : 1)[a]		4.62	62.4	3.1	34.5	1.81
$NO_2^+PF_6^-$-dimethyl sulfide (1 : 2)[a]		65.73	62.3	3.3	34.4	1.81

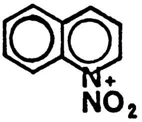
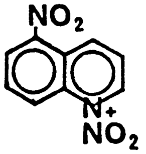
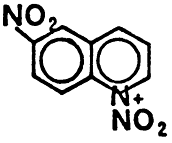
[a] In nitroethane at -78°.

TABLE IX COMPETITIVE NITRATION OF BENZENE AND TOLUENE WITH N-NITROPYRIDINIUM (QUINOLINIUM) SALTS AT 25° (CUPAS AND PEARSON (25)

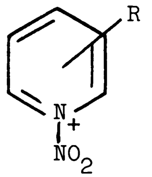
N-Nitro Salt	Solvent	Isomer Distributions %O	%M	%P	K_T/K_B
	$CH_3C{\equiv}N$	63.8	3.2	33.0	36.5
	$CH_3C{\equiv}N$	62.9	3.0	34.1	40.5
	$CH_3C{\equiv}N$	63.0	2.7	34.3	46.4
	$CH_3C{\equiv}N$	63.9	3.0	33.1	39.0

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

TABLE IX (continued)

N-Nitro Salt	Solvent	Isomer Distributions			K_T/K_B
		%O	%M	%P	
	$CH_3C{\equiv}N$	62.4	3.5	33.1	32.6
	CH_3NO_2	62.1	2.1	35.8	13.2
	CH_3NO_2	61.4	2.2	36.4	14.5

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001



R = -H, -CH_3, -OCH_3

Friedel-Crafts Nitrations

The general Friedel-Crafts acylation principle (26) can be applied easily to inorganic acid halides and anhydrides. Consequently, it seems proper that aromatic nitrations involving nitryl halides, dinitrogen pentoxide and dinitrogen tetroxide (the halides and anhydrides of nitric acid) should be considered as Friedel-Crafts type reactions, as obviously a very close analogy exists with the corresponding Friedel-Crafts ketone syntheses involving acyl halides and anhydrides (27). In a generalized sense, nitric acid nitrations catalyzed by protonating acids (H_2SO_4, H_3PO_4, HF, etc) or by Lewis acid type metal halides (BF_3, $AlCl_3$, etc) could be also considered as reactions of Friedel-Crafts type, as an increasing number of Friedel-Crafts ketone syntheses is now known using aliphatic carboxylic acids (acetic, propionic, etc) as acylating agents.

Nitration with Nitryl Chloride. Friedel-Crafts type nitration using nitryl chloride has been previously reported by Price and Sears (28) who found $AlCl_3$ to be the most suitable catalyst. Deactivated aromatics, however, were nitrated only with difficulty and the method was, therefore, considered to be of limited value.

Our investigations with Kuhn (29) have shown that aromatic compounds, including deactivated ones such as halobenzenes and benzotrifluoride, can be nitrated with ease using nitryl halides and a suitable Friedel-Crafts catalyst.

$$ArH + NO_2X \longrightarrow ArNO_2 + HX \quad (X = F, Cl, Br)$$

Using nitryl chloride as the nitrating agent, which in the laboratory is conveniently prepared by the reaction of nitric acid with chlorosulfuric acid (30), $TiCl_4$ was found to be the most suitable catalyst. $FeCl_3$, $ZrCl_4$, $AlCl_3$ and $AlBr_3$ are also effective but the reactions are more difficult to handle. With BCl_3 we obtained a smaller amount of nitrated product and considerable ring chlorination; SbF_5 is also an active catalyst for the nitryl chloride nitration of aromatics; BF_3 was found to be inactive as a catalyst. The following yields were obtained upon nitration of the aromatics using $TiCl_4$ as catalyst: benzene 88%, toluene 81.5%, ethylbenzene 79%, fluorobenzene 91%, chlorobenzene 41.5%, benzotrifluoride 32%. There is always a certain amount

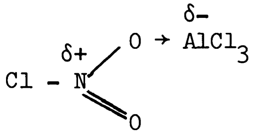
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

of ring chlorinated by-product formed in the nitrations. Reactions carried out either by using an excess of aromatics as solvent ($TiCl_4$ is miscible with many aromatics) or in carbon tetrachloride solution, always contain chlorinated by-products. The amount of chlorinated by-products can be decreased by using solvents of higher dielectric constants. Tetramethylene sulfone (sulfolane) was found to be a suitable solvent for the $TiCl_4$ and also for most of the other Lewis acid-catalyzed nitrations. It has excellent solvent properties for aromatics and the catalysts, as well as for nitryl halides. It is superior to other solvents that can be used, such as nitromethane. As it is completely miscible with water, the work-up of the reaction mixtures after the reactions are completed is very easy.

In Lewis acid halide catalyzed nitrations with nitryl chloride the question arises are these reactions nitronium salt nitrations according to the ionization

$$NO_2Cl + AlCl_3 \rightleftharpoons NO_2^+AlCl_4^-$$

or are they effected by the O-coordinated donor:acceptor complex



In order to study this problem, we carried out with Lin (13) competitive studies of nitration of benzene and toluene with nitryl chloride, catalyzed by Lewis acid halides. When excess aromatics was used as solvent, the data summarized in Table X were obtained. The data show that the substrate selectivity changes from 11 to 39, accompanied by small changes in isomer distribution. Generally the *ortho/para* ratios are smaller than in nitrations with nitronium salts. In general as stronger the acid catalyst, the lower the k_T/k_B ratio. The stronger catalyst forms a more polarized complex resembling more the nitronium salt. The observed changes, however, point to the fact that the nitrating agents are the corresponding donor:acceptor complexes and not the nitronium ion itself. The lower *ortho:para* ratios than those obtained in case of NO_2^+, particularly point to bulkier nitrating agents.

However, when carrying out the reactions in a common polar, ionizing solvent, such as nitromethane, such factors are diminished as shown in Table XI.

Nitrations with Nitryl Fluoride. Nitryl fluoride is a more powerful nitrating agent than nitryl chloride, but is more difficult to handle. Hetherinton and Robinson (31) reported nitration of aromatics with nitryl fluoride, in the absence of catalysts. They suggested, that in solution, nitryl fluoride dissociates into NO_2^+ and F^- and the intermediate nitronium ion thus formed is the

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

TABLE X

LEWIS ACID HALIDE CATALYZED FRIEDEL-CRAFTS NITRATION OF BENZENE AND TOLUENE WITH NITRYL CHLORIDE AT 25°

Lewis acid halide	$k_{toluene}/k_{benzene}$	Isomer distribution, % ortho	meta	para	o/p
$AlCl_3$	11.2	53.3	1.2	45.5	1.17
$TiCl_4$	17.6	53.1	1.6	45.4	1.17
BF_3	25.1	57.4	1.4	41.1	1.40
$SbCl_5$	26.7	56.4	1.4	42.2	1.34
PF_5	39.3	57.6	1.6	40.8	1.41

TABLE XI

LEWIS ACID HALIDE CATALYZED FRIEDEL-CRAFTS NITRATION OF BENZENE AND TOLUENE WITH NITRYL CHLORIDE IN NITROMETHANE SOLUTION AT 25°

Lewis acid halide	$k_{toluene}/k_{benzene}$	Isomer distribution, % ortho	meta	para	o/p
$AlCl_3$	26.8	61.3	3.7	35.0	1.75
$TiCl_4$	27.8	61.1	3.7	35.2	1.74
PF_5	28.5	61.6	3.5	34.9	1.76

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

active reagent in the nitrations. Less reactive aromatics such as nitrobenzene were not nitrated and considerable tar formation occurred during the reactions. We found that by using a Lewis acid type fluoride catalyst such as BF_3, PF_5, AsF_5 and SbF_5, simple Friedel-Crafts type nitrations can be carried out with nitryl fluoride (29). Homolytic cleavage of nitryl fluoride, which causes most of the side reactions, is considerably suppressed under these conditions in favor of heterolysis, yielding the nitronium ion. The reactions are carried out preferably at low temperatures. Benzotrifluoride is nitrated to m-nitrobenzotrifluoride at -50° with 90% yield using boron trifluoride as catalyst. Halobenzenes, including di- and polyhalobenzenes, are nitrated with ease and with yields of over 80%.

The nitrations are carried out either with an excess of the aromatic as diluent and introducing nitryl fluoride and the Lewis acid fluoride catalyst simultaneously at low temperature into the well stirred reaction mixture or in a suitable solvent such as tetramethylene sulfone which can be used as solvent advantageously if the catalyst fluoride does not interact with it (SbF_5 being a strong fluorinating agent, attacks the solvent and cannot be used).

Nitrations with Nitryl Bromide. Nitryl bromide compared with the chloride and fluoride, is quite unstable. Nitration experiments were carried out with solutions obtained by the halogen exchange of nitryl chloride with KBr (not separated from unchanged nitryl chloride and decomposition products) carried out in sulfur dioxide solutions at -20°, and using $TiBr_4$ as catalyst. Yields of nitrations are lower than those obtained with nitryl chloride, due to the formation of more ring-brominated products (29). This can be attributed partly to free bromine being present from the decomposition of nitryl bromide and to the easier homolysis of nitryl bromide itself.

Nitrations with Dinitrogen Tetroxide. It was Schaarschmidt (32) who first investigated the catalytic effect of $AlCl_3$ and $FeCl_3$ on nitration of aromatics with N_2O_4, the mixed anhydride of nitric and nitrous acids.

Pinck (33) used sulfuric acid to catalyze the nitration of aromatics with N_2O_4. He observed that only half of the dinitrogen tetroxide was used up in the nitrations, the remainder being present as nitrosylsulfuric acid. Titov (34) dissolved N_2O_4 in sulfuric acid and used this solution as nitrating agent.

Raman spectroscopic (35) and cryoscopic (36) investigations of solutions of N_2O_4 in sulfuric acid gave proof that the effective nitrating agent in the solutions is the nitronium ion (NO_2^+) and also explained

$$N_2O_4 + 3H_2SO_4 \rightleftharpoons NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

the formation of an equimolar amount of nitrosyl sulfuric acid ($NO^+HSO_4^-$).

Bachman (37) used the stable $N_2O_4 \cdot BF_3$ complex prepared as a crystalline, insoluble salt from the components in aromatic nitrations. He suggested a nitronium salt structure for the complex

$$(NO_2^+)(F_3B\text{-}NO_2^-)$$

The crystalline complex, however, is only a moderate nitrating agent giving sufficient yields in nitrations of even such reactive aromatics as benzene and naphthalene only after long reaction times (24 hours to one week). This obviously is not in agreement with the suggested nitronium ion structure. Also the $N_2O_4 \cdot BF_3$ complex shows an ability to nitrosate and diazotize , thus acting also as a nitrosonium salt

$$(NO^+)(F_3B\text{-}NO_3^-)$$

Raman spectroscopic investigations of the solid complex, carried out with John Evans (38) showed only a relatively weak band at 1400 cm^{-1}, but a strong one around 2340 cm^{-1}. It was therefore, suggested that the addition compound $N_2O_4 \cdot BF_3$, which is not necessarily completely ionized in the solid state, can form an equilibrium mixture of the nitronium and nitrosonium forms in agreement with its observed reactivity and the fact that N_2O_4 itself is the mixed anhydride of HNO_3 and HNO_2.

The major difficulty in Friedel-Crafts type nitrations with N_2O_4 was previously the fact that the N_2O_4-catalyst complexes were insoluble in the reaction media. This resulted not only in slow reactions and low yields, but also in many cases in undesirable side reactions.

Schaarschmidt reported that when $AlBr_3$ was tried instead of $AlCl_3$ as a catalyst, in an unexpected way only ring bromination took place and no nitro product was formed. The use of a fluoride catalyst, such as BF_3 in the work of Bachman, eliminated halogenation as side reaction but still dealt with a heterogeneous reaction medium.

In the course of our investigation, we found that homogeneous Friedel-Crafts type nitrations with N_2O_4 and Lewis acid catalyst such as $TiCl_4$, BF_3, BCl_3, PF_5 and AsF_5 can be carried out in tetramethylene sulfone solutions. It is not necessary to isolate the catalyst-N_2O_4 complex. Instead, a solution of N_2O_4 and the catalyst is prepared and this solution is added to a tetramethylene sulfone solution of the aromatic to be nitrated.

Nitrobenzene was obtained from the nitration of benzene with yields of 32-67%, fluoronitrobenzenes from fluorobenzene with 28-76% yields, the relative order of activity of the catalysts used being $AsF_5 > PF_5 > BF_3 > TiCl_4 > BCl_3$. With the chloride catalysts used, a considerable amount of chlorobenzene also was formed in the reaction, as was the case with $AlCl_3$.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Bromide Lewis acids such as $AlBr_3$, BBr_3 and $TiBr_4$, in agreement with previous observations of Schaarschmidt with $AlBr_3$, gave a high amount of ring bromination but simultaneously also about 10% of nitroaromatics were formed.

Subsequent investigations have proved that aluminum, titanium and boron halides tend to react with N_2O_4 in the following way

$$2N_2O_4 + TiCl_4 \rightarrow 2NO_2Cl + 2NOCl + TiO_2$$

$$3N_2O_4 + Al_2Br_6 \rightarrow Al_2O_3 + 3NO_2Br + 3NOBr$$

$$3N_2O_4 + 2BBr_3 \rightarrow B_2O_3 + 3NO_2Br + 3NOBr$$

NO_2Br, being unstable, decomposes to N_2O_4 + Br_2 and the bromine formed in the presence of the catalyst brominates the aromatic. In a similar manner, but to a lesser extent, chlorination takes place with chloride catalysts.

Nitrations with Dinitrogen Pentoxide. Nitrations using nitrogen pentoxide, the anhydride of nitric acid, are well known (39). Most of the work was carried out in solution in the absence of catalyst. Solid nitrogen pentoxide at low temperatures is known to be nitronium nitrate, NO_2^+ NO_3^-. A study of the kinetics and mechanism of nitrogen pentoxide nitrations gave evidence, however, for the fact that other carriers of the nitronium ion may also play a role. Decomposition of N_2O_4 and oxygen should also be considered if the N_2O_5 used is not entirely pure.

Klemenz and Scholler (40) have shown that solutions of N_2O_5 in sulfuric acid are very effective nitrating agents having nitrating properties similar to those of solutions of nitric acid in sulfuric acid.

Millen (41) found the ionization of N_2O_5 in sulfuric acid to be

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + 3HSO_4^- + H_3O^+$$

Bachman (42) reported on the use of the stable insoluble $N_2O_5 \cdot BF_3$ complex in aromatic nitrations, the active nitrating agent being $NO_2^+BF_3ONO_2^-$. We have found in our investigations that N_2O_5 can be used as a very effective nitrating agent in Friedel-Crafts type nitrations in the presence of Lewis acid catalysts such as BF_3, $TiCl_4$, $SnCl_4$ and PF_5 in tetramethylene sulfone solution. It is not necessary to isolate the intermediate N_2O_5-Lewis acid complexes as the solutions of N_2O_5 and the catalyst can be well controlled in homogeneous solutions. In general, the solution of N_2O_5 and the Lewis acid catalyst (in equimolar quantities) is run into the stirred and cooled solution of the aromatic in tetramethylene sulfone. After the addition is completed, the mixture is allowed to come to room temperature and is then stirred for another 15 minutes. Alkylbenzenes (benzene, toluene, xylene,

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

ethylbenzene, propylbenzene butylbenzene, mesitylene) were nitrated with yields of 87-95%. As the reactions are carried out in homogeneous media, the amount of dinitro products is negligible if an excess of alkylbenzene is used. Halobenzenes (fluoro-, chloro-, bromo- dihalobenzenes, benzotrifluoride) were nitrated with yields of 79-89%.

When the N_2O_5 nitration is carried out in liquid anhydrous HF as solvent (which does not appear to react with N_2O_5 at a temperature below 0°) using a catalyst such as BF_3, SbF_5, PF_5, AsF_5, SiF_4, NbF_5, WF_6, etc, a quantitative formation of the corresponding nitronium salts takes place. As HF also acts as a good ionizing solvent, an extremely active nitration medium is obtained. Nitrobenzene and benzotrifluoride are nitrated with yields of over 90% at temperatures between -20 and 0°.

One of the difficulties of using anhydrous HF as solvent (aside from some inconveniences arising from its being handled in laboratories not equipped for fluorine work) is the fact that it is a rather poor solvent for aromatic (solubilities are generally less than 2%) and, therefore, the reactions must be carried out by vigorous stirring of the heterogeneous reaction mixtures. The use of pyridinium polyhydrogen fluoride, a convenient HF like solvent, overcomes much of these difficulties.

Nitration with Alkyl Nitrates

In our studies of electrophilic nitrations, we also found alkyl nitrates, particularly methyl nitrate, very effective nitrating agents in the presence of boron trifluoride as catalyst (43,44).

$$ArH + NO_2OCH_3 \xrightarrow{BF_3} ArNO_2 + CH_3OH{\cdot}BF_3$$

The reaction was found particularly useful as a relatively selective and mild nitration method, for example allowing mononitration of durene and other highly alkylated benzenes, which with mixed acid usually undergo dinitration. (Table XII). Methyl nitrate-boron trifluoride can also be used to achieve dinitration of tetramethylbenzenes by using two and three molar excess of methyl nitrate, respectively. Relative yields of mono- and dinitro product compositions are shown in Table XIII. Other Friedel-Crafts type catalysts can also be used, but boron trifluoride was found to be the most suitable. Aluminum trichloride and titanium (IV) chloride in the nitration of pentamethylbenzene caused formation of significant amounts of chlorinated derivatives, whereas sulfuric acid led to nitrodemethylation products.

Methyl nitrate-boron trifluoride in nitromethane solution, as discussed, is a selective nitrating agent, which gave exceptional yields in the mononitration of polymethylbenzenes. In the reaction alcohol (methyl alcohol) is formed as by-product, which is

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

TABLE XII.

Boron Trifluoride Catalyzed Mononitration of Polymethylbenzenes with Methyl Nitrate in Nitromethane Solution

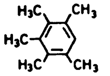
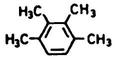
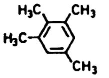
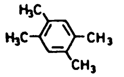
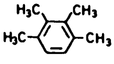
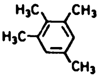
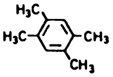
Polymethylbenzene	Yield (%) of Isolated Mononitro Product
	99
	95.4
	97.5
	97.0

TABLE XIII.

Boron Trifluoride Catalyzed Nitration of Tetramethylbenzenes with Excess Methyl Nitrate in Nitromethane Solution

Tetramethylbenzene	$H_3C—ONO_2$: Arene	Total yield (%) of nitro products	Composition	
			Dinitro product (%)	Mononitro product (%)
	2:1	93	64.4	35.6
	3:1	90	75.0	25.0
	2:1	94	89.9	10.1
	3:1	94	99.9	0.1
	2:1	95	90.1	9.9
	3:1	92	100	0

then complexed by boron trifluoride catalyst. Usual mixed acid nitrations give water as the by-product in forming the nitronium ion. Nitric and sulfuric acid under nitrating conditions can also be strong oxidizing agents causing particularly in polynitrations, such as the preparation of TNT and TNB, substantial losses due to oxidative cleavage reactions. In our studies we have found that using HF-BF_3 as the acid medium (which forms the nitronium ion with BF_3 binding water) generally minimizes oxidative side reactions.

The effectivness of mixed acid is well known to continously decrease during the progress of the nitration reaction due to dilution of the acid by the water formed. We have found that a mixture of nitric and fluorosulfuric acid is a highly enhanced reactivity nitration medium, allowing for example easy trinitration of benzene directly to 1,3,5-trinitrobenzene (23). Water formed in the ionization of nitric acid to the nitronium ion is reacting with fluorosulfuric acid, thus the medium is self dehydrating and maintains high activity.

The use of nitronium ion salts, Friedel-Crafts nitration systems, and their combination allows the easy and generally very high yield nitration of practically any conceivable aromatic substrates. The reactions can also be extended from mononitration with relative ease to di- and trinitration, providing greatly improved preparative methods for such significant products as dinitrotoluenes and xylenes, trinitrotoluene, and trinitrobenzene.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Mechanistic Aspects

Aromatic Nitration. Ingold's fundamental studies in the 1940's which established our understanding of electrophilic nitrations, concluded concerning the nature of the nitrating agent for all nitrations the reactive nitrating agent is the nitronium ion, NO_2^+ (2). Other species such as the nitracidium ion $H_2NO_3^+$ were considered, but rejected primarily because no such species were ever observed directly by spectroscopic or other means. Kinetic studies have shown that with reactive substrates the formation of the nitronium ion is the slow, rate limiting step, and nitration of the aromatic substrates show pseudo zero-order. With increasingly less reactive substrates, or by decreasing the acidity of the system, rates were shown to change to first-order in aromatics, indicating that now the interaction of the nitronium ion (present in the system in a steady-state equilibrium) with the aromatics is becoming rate limiting.

When in our nitration studies in the 1950's, we were able to work out effective methods for the preparation of nitronium salts, particularly the tetrafluoroborate and use them as a nitrating agent (4), our assumption in ensuing mechanistic studies was that we can eliminate the first two steps of the Ingold kinetic scheme

$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O$$

$$ArH + NO_2^+ \rightleftharpoons ArHNO_2^+$$

$$ArHNO_2^+ \longrightarrow ArNO_2 + H^+$$

and thus directly study the interaction of the nitronium ion with the aromatics (45). As the nitration of benzene and toluene is generally too fast to be measured by noncompetitive rate studies, Ingold used Wibaut's originally developed competitive method of rate determination (46). This method was also used in our studies.

Low Substrate and High Positional Selectivity. Nitrations with nitronium tetrafluoroborate in nitromethane and nitronium hexafluorophosphate in nitromethane solution, respectively, show low substrate selectivities (generally expressed by the k_{Ar}/k_B rate ratios) but at the same time the nitrations maintained high positional selectivity. Typical isomer distributions in the nitration of toluene are 67% ortho, 4% meta, and 29% para nitrotoluene. The data summarized in Table XIV show the relative reactivities of a number of alkylbenzenes over those of benzene, together with the isomer distributions of the mononitro products.

TABLE XIV

COMPETITIVE NITRATION OF ALKYLBENZENES AND BENZENE WITH NO_2BF_4 IN TETRAMETHYLENE SULFONE SOLUTION AT 25°

Ar	$k_{Ar}/k_{benzene}$	Isomer distribution, %			*ortho:para* ratio
		ortho	*meta*	*para*	
Benzene	1.00				
Toluene	1.67	65.4	2.8	31.8	2.05
o-Xylene	1.75	3-Nitro-*o*-xylene, 79.7% 4-Nitro-*o*-xylene, 20.3%			
m-Xylene	1.65	2-Nitro-*m*-xylene, 17.8% 4-Nitro-*m*-xylene, 82.2%			
p-Xylene	1.96				
Mesitylene	2.71				
Ethylbenzene	1.60	53.0	2.9	44.1	1.20
n-Propylbenzene	1.46	51.0	2.3	46.7	1.09
i-Propylbenzene	1.32	23.4	6.9	69.7	0.34
n-Butylbenzene	1.39	50.0	2.0	48.0	1.04
t-Butylbenzene	1.18	14.3	10.7	75 0	0.19

It is obvious from the data summarized in Table XIV that whereas positional selectivity remained high, the substrate selectivity is very low (for all alkylbenzenes studied compared to benzene, it ranges from 1.3 to 2.7). Studied alkylbenzenes seem to have reached a more or less limiting value, and therefore, no significant substrate selectivity differences can any more be considered (see subsequent discussions of Schofield's views on

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

encounter controlled rates).

We stated in our original paper: "The method of competitive reaction rate determination can be applied only if the observed relative rates are dependent on the aromatic substrate. As our observed relative rates showed only low selectivity concerning the nature of the aromatic substrate it could have been attributed to a very fast reaction taking place when the solution of nitronium salt reagent is dropped into the solution of the mixed aromatic substrate. Thus the NO_2^+ ion would have no possibility of reaching uniform distribution in the solution before reaction occurs with the aromatics and observed relative rates may be influenced rather by statistical factors than real competition". In order to clarify this possibility and also to determine the accuracy of the method used, we carried out experiments to establish whether real competitive reaction actually occured under our experimental conditions and whether the methods employed provided results which could establish small differences between the alkylbenzenes investigated (11).

The studies directed to clarify this point included variation of changeable parameters, including the efficiency and speed of stirring, change of solvent, change of temperature etc, as well as changing the concentration of both of the aromatic components in competitive experiments.

Data of nitration of benzene and toluene (as well as alkylbenzenes) represented a puzzle at the time in the interpretation of an electrophilic aromatic substitution reaction. The application of the Hammett $\sigma\rho$ relationship to aromatic substitution by Brown, generally known now as the "Brown selectivity relationship" (47) would predict that as more reactive a reagent, the lesser the substrate, but also the positional selectivity. In other words, with very reactive reagents, toluene and benzene would give little reactivity difference but, at the same time the three competing positions in toluene (ortho-meta-para) also will tend to lose selectivity, and in the limiting case statistical, i.e., 40% ortho, 40% meta, 20% para substitution would be expected. In other words, with increasingly reactive reagents, low substrate and low positional selectivities, reflected by high meta isomer ratios, are expected to be observed. This certainly was not the case in the nitronium salt nitration of toluene, which can be classified as a low substrate, but high positional selectivity nitration. To account for the experimental data, the only explanation we were able to offer was, that in the reaction the transition state of highest energy lies early on the reaction coordinate, being of molecularly bound π-complex nature. In a subsequent step, representing a separate energy barrier, the corresponding ortho, meta, and para arenium ion like transition states are formed, leading to the isomeric products.

That, indeed, with highly reactive nitrating agents statistical substitution can take place was shown when carrying out free-radical nitration of benzene and toluene, for example, with N_2O_4

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

in light, and with peroxides to produce $NO_2\cdot$. We obtained the following nitrotoluene isomer distribution and relative rate ratio

$k_T:k_B$ = 2.6; ortho 37.2%; meta 38.1%; para 24.7%

Similar results were obtained in the thermal nitration of toluene and benzene with tetranitromethane (23).

$k_T:k_B$ = 0.7; ortho 41.5%; meta 39.1%; para 19.4%

Data indicate the predominately statistical nature of the reaction, with the isomer distribution coming close to the expected 40% ortho, 40% meta and 20% para isomer values (49).

These data clearly show that low substrate and low positional selectivity nitration reactions, can indeed, take place. The high reactivity of the reagent is responsible for low selectivity concerning both substrates and positions. These reactions are, however, very different from the observed nitronium salt nitrations in which positional selectivity stays high.

Our mechanistic concept was criticized (50) on exactly the basis we raised ourself previously and thoroughly studied, i.e., that the competitive method used was insufficient in case of fast reactions where the rate of the interaction with the substrates may have exceeded that of mixing. Obviously in fast nitrations mixing can become a serious factor, as shown by Ridd (51) in the case of NO_2^+ salt nitration of bibenzyl. In studied nitrations of toluene and benzene difficulties caused by incomplete mixing before reaction is, however, not the only reason for the findings (21). This was shown by the relatively limited amount of dinitration observed (45,49), by experiments of Ritchey using competing four components (52), studies using methods such as mixing the reagents in an efficient stopped-flow reactor system (13,53), but more significantly by the fact, that substrate selectivity of the nitration of benzene and alkylbenzenes clearly vary with the nitrating medium. Ingold himself found small differences for the relative rate of nitration of toluene and benzene for nitric acid in acetic anhydride (k_T/k_B = 23) and nitric acid in nitromethane (k_T/k_B = 21). More significant differences were found when carrying out the reactions in acid mixtures of varying strength, for example 68% sulfuric acid (k_T/k_B = 17), 61% perchloric acid (k_T/k_B = 19), 7.5% aqueous sulfolane (k_T/k_B = 20), and 15% aqueous nitromethane ($k_T:k_B$ = 25). The spread of k_T/k_B in these studies varies from 17 to 25 thus represents a $\sim$ 35% difference. That this difference cannot be simply attributed to experimental uncertainty is obvious when one compares similar data for other alkylbenzenes in the same media. Generally the observed differences are even larger and point to the same direction. The media thus, not unexpectedly, significantly affects the reactivity of the nitrating system and consequently the substrate selectivities.

The concern over the reliability of the small substrate sel-

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

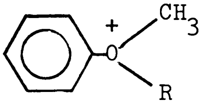
ectivity numbers found in our work with nitronium salt nitration and their criticism labelling them in the extreme as meaningless and caused exclusively by "mixing control" (see for example L.M. Stock's paper at this Symposium), should, however, not obscure the fact, the intermolecular substrate selectivity does, indeed, vary with the nitrating medium. Even more significant are, however, the variations in intramolecular, positional selectivity (i.e., isomer distributions), which of course, cannot be affected by any stretch of imagination by "mixing control". They show similar significant changes. The frequently quoted invariability of isomer distributions in the nitration of toluene, which supposedly proves that always a common nitrating agent (i.e., the NO_2^+) is involved, and further the activity of this reactive electrophile is not affected by changing the reaction medium, cannot be further maintained. Inspection of data of Table XV should make this point clear.

TABLE XV. Isomer Distribution in Nitration of Toluene

Nitrating agent	Solvent	Temp °C	%ortho	%meta	%para	ortho/ para
$NO_2^+PF_6^-$	CH_3NO_2	25	68	2	30	2.27
$NO_2^+BF_4^-$	sulfolane	25	66	3	31	1.94
HNO_3	Ac_2O	30	58	4	38	2.13
HNO_3	AcOH	25	57	3	40	1.42
HNO_3	CCl_4	25	53	3	44	1.20
$NO_2Cl{\cdot}TiCl_4$	-	25	53	2	45	1.18

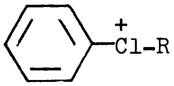
Whereas it could be argued, that the isomer distribution differences in the nitration of toluene are not large (see, however, the 50% variation in ortho/para ratios in Table XV) these differences are becoming much more significant when comparing data of nitrations in similar media for o-xylene, anisole, and chlorobenzene (TABLE XVI).

In our studies we found no specific ortho directing effect due to the n-donor nature of CH_3O- or Cl- substituents through initial attack by the nitrating agent on the hetero-atom of the substituent. As a matter of fact when oxonium or halonium ions of the type



or

R=alkyl



Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

TABLE XVI

ISOMER DISTRIBUTION IN NITRATION OF CHLOROBENZENE,
ANISOLE, AND o-XYLENE

Nitrating agent	Solvent	%ortho	%meta	%para	ortho/para
Chlorobenzene					
$NO_2^+PF_6^-$	CH_3NO_2	31	1	68	0.46
HNO_3	H_2SO_4	30		70	0.43
HNO_3	Ac_2O	20.5		79.5	0.26
HNO_3	AcOH	19.4		80.6	0.24
$AsONO_2$	CCl_4	15		85	0.18
Anisole					
$NO_2^+BF_4^-$	sulfolane	73	<0.2	27	2.70
HNO_3	AcOH	44	<1	55	0.80
$CH_3ONO_2 \cdot BF_3$	CH_3NO_2	28	<1	71	0.39

o-Xylene		%3-nitro	%4-nitro	3-/4-nitro
$NO_2^+BF_4^-$	sulfolane	75	25	3.0
$CH_3ONO_2 \cdot BF_3$	CH_3NO_2	58	42	1.38
HNO_3	Ac_2O	35	75	0.47
HNO_3	49% H_2SO_4	31	69	0.45

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

where de facto prepared, transfer of R substituent into the aromatic ring was found entirely an intermolecular process for both anisole and chlorobenzene. Thus, the high ortho/para isomer ratios in case of anisole, having an electronic effect of + K >> - I are considered normal for a strongly electrophilic reagent, whereas increasing selectivity results in increasing para substitution. Chlorobenzene (- I > + K) shows, as expected, a lesser trend, but in the same direction.

The results of nitration of anisole are particularly revealing. With nitronium tetrafluoroborate high ortho/para isomer ratio (2.70) is obtained not accompanied by formation of any detectable amount of meta isomer! Substrate selectivity is at the same time low, both anisole and benzene reacting with the very reactive nitronium salt with about the same limiting rate. Using, however, a more selective nitrating system, such as the BF_3 catalyzed nitration with methyl nitrate in nitromethane solution, para substitution is becoming predominant (ortho/para - 0.39), at the same time substrate selectivity is becoming much higher ($k_A/k_B = 187$).

These data are not in accord with a $\sigma^+\rho^+$ type linear relationship, which would predict that an energetic reagent should give low substrate, but also at the same time positional selectivity. The assumption implicit in the $\sigma^+\rho^+$ relation, that the direct resonance effects of substituents (such as the methoxy group) can be represented by a single constant, thus clearly cannot be further accepted.

To reconcile the experimental findings, the following depiction of the reaction mechanism of electrophilic aromatic nitration can be given. In order to explain the low substrate but high positional selectivities observed in highly exothermic electrophilic aromatic nitrations with nitronium salts, it is necessary to suggest that in these reactions the transition state of highest energy leads to formation of a molecularly bound π-complex (in the substrate selectivity determining step), followed by formation of σ-complexes for the ortho, para, and meta positions, which differ significantly in energy. Figure 1a depicts the potential energy curve for such a reaction (for simplicity only reactions displaying no kinetic hydrogen isotope effects are shown).

In contrast Figure 1b depicts the energy diagram of less energetic nitrating agents (acetyl nitrate or methyl nitrate) in the case where formation of the σ-complexes is the rate limiting step of the reaction. (The possible importance of proton elimination on the right side of the energy curves is for simplicity not emphasized; see, however, the subsequent discussion of the role of kinetic hydrogen isotope effects.)

On the reaction path of aromatic nitration the initial interaction of the reactive nitrating agent (NO_2^+) with activated aromatic substrates leading to π-complex (benzonium ion) formation can involve a low energy barrier (2-3 kcal/mol) as the highly energetic NO_2^+ provides the excess energy.

The bonding interaction involves the highest lying occupied

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

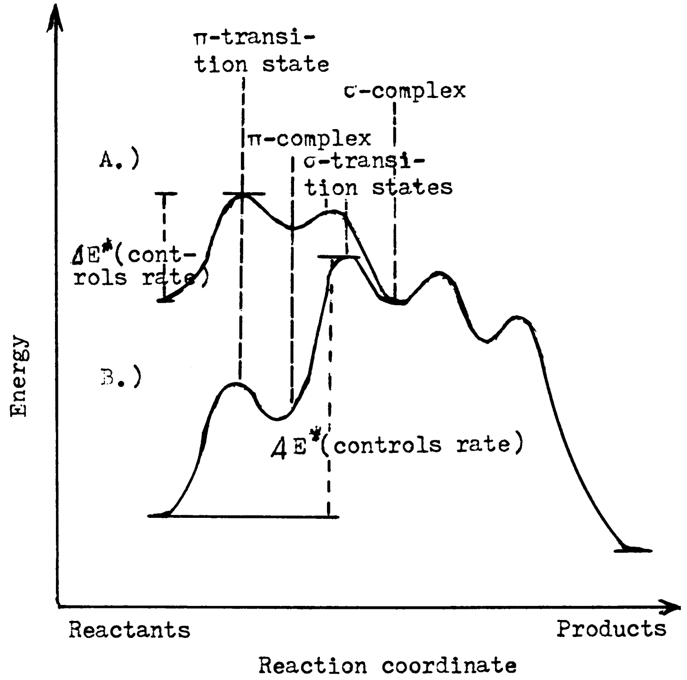
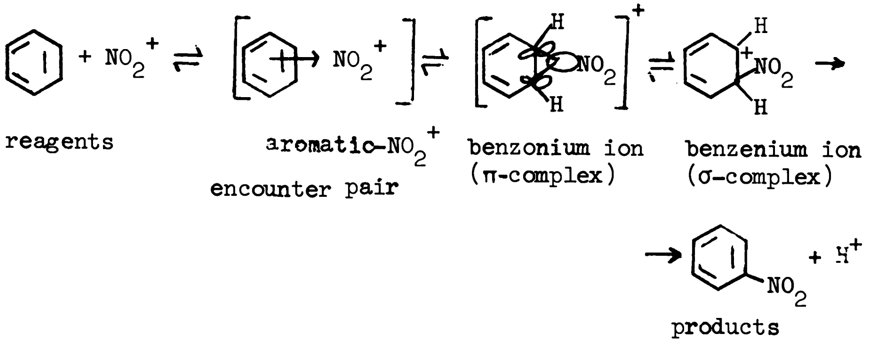


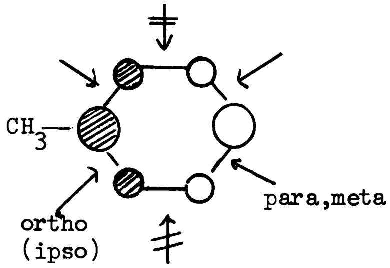
Figure 1. Energy Diagram for Aromatic Nitration *with A.) highly energetic nitronium salts, B.) more selective nitrating agents (acetyl or methyl nitrate)*

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

aromatic π-orbital, containing an electron pair, overlaping with the developing bonding orbital of the electrophile, forming a two-electron, three-center bond (molecularly bound π-complex). The formed bridged tetracoordinated carbonium ion (benzonium ion)(54) then through opening of the three-center bond gives the trivalent benzenium ion (σ-complex) which frequently can be directly observed.



Concerning directing effects, as in the case of the methyl group in toluene, consideration of the symmetry of the highest occupied molecular orbital (HOMO) involved in the interaction with the electrophile (NO_2^+) gives good indication. As interaction can take place only on bonds formed by orbitals bearing the same sign, *i.e.*, 1-2, 1-6, 3-4, and 4-5, but not 2-3 and 5-6, attack on the two former can lead only to ortho (or ipso) substitution, whereas the latter will give *para-* (and less *meta-*) substituted products (55).



Isomer distributions in reactions involving product determining transition states lying also relatively early on the reaction coordinates, will resemble more the π-bonded benzonium ions, and not the benzenium ions. Charge distribution calculations of the related HOMO's of the aromatics as well as of the corresponding arenium ion complexes are in full accord with this picture. The latter are the more stabilized for the para substituted isomers, while in the former charge distribution are higher around the ortho positions. Meta substitution is not favored in any case and it is indeed never becoming significant under kinetically controlled conditions.

When relating intermediates, such as the well studied and identified σ-complexes, to transition states of the reactions, it should be realized that the Hammond postulate in multi-step reacting can be applied only to transition states directly proceeding the intermediates and cannot relate to other, further lying transition states separated by reaction minimia. If another intermediate is higher lying than the more stable arenium ion, it will not be generally observable, which however does not effect its involvement on the reaction path of a multi-step process.

It is clear from the foregoings that the molecularly bound benzonium ion (π-complex) with opening of the three-center bond transfers into the corresponding benzenium ions (σ-complexes). When considering this process at a bond at which the carbon atom carrying the initial substituent is attached, it is obvious that besides the ortho-nitrobenzenium ions also the so-called "ipso" substituted ion should be formed. Ipso attack thus is in my view not a special case, but, indeed an integral part of all aromatic substitution reactions. The only difference is that in order to de facto observe ipso substitution, the original substituent must be of a good electrophilic leaving group nature. In the case of toluene this is not the case, as CH_3^+ would be the most unsuitable leaving group. With other more suitable substituents, however, ipso nitration is quite feasible and recently much studied (56). It should be recalled, that what is now called an ipso nitration of isomeric cymenes and para-tertiary butyltoluene, for example, were known for many decades (57). Anomalaous ciné-nitrations (58) (meaning that the substituting agent ends up at a position other than the departing group) are also easily rationalized with the general scheme of the substitution process and possible concurrent or consecutive isomerizations.

Our suggestion that aromatic nitration with the nitronium salts proceeds through a reaction path involving separate π- and σ-complex like transition states was since also indicated in many other electrophilic aromatic substitutions. In the late 1960's Coombes, Moodie, and Schofield (63) found in their study of kinetics of nitration in varying strengths of sulfuric-nitric acid mixtures, that in acids more concentrated than 68.3%, the reactions of reactive aromatics such as toluene and alkylbenzenes proceed with what they termed encounter rate control. Considering the fact that nitronium ion nitrations carried out in non-aqueous low nucleophilicity solvents represent a much more reactive system, benzene, as well as toluene and alkylbenzenes, can react with the same limiting rate. The studies of Schofield, Moodie, and Coombes in my view are thus not contradictory to our nitronium salt nitration data, when considering the formation of the so called encounter pair as a separate intermediate, similarly to the early π-complex suggested in our work, both species preceding the σ-complex

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

intermediates. However, to term these processes as entirely diffusion controlled, is at least in my opinion difficult to fully accept. Bimolecular reactions with exception perhaps of acid-base neutralization reactions, are rarely completely diffusion controlled. Furthermore, the nitronium ion although a reactive electrophile, is certainly not more reactive than carbenium ions or other strong electrophiles. If the suggestion for diffusion control in nitration would be correct, then similar control should be also indicated for all other electrophilic aromatic substitutions showing similar selectivity patterns. This is, however, not the case, as in a series of other substitution reactions non-competitive rate measurements are possible, and, indeed, were carried out.

The only possible explanation to exclude rate limiting π-complex formation of nitronium salt nitrations showing high positional selectivity, such as toluene, would be, as suggested by Schoefield, if the reaction at the more activated ortho and para positions would take place at fast encounter rate, but not at the relatively less reactive meta position. We already discussed the question, that there is little reason that benzene, or for this reason, the meta positions in toluene, should show such a basically differing behavior. This can, however, further be excluded when considering the case of o-xylene. Obviously, both the activated 3- and 4-positions should, according to Schofield's concept, react at encounter rate. The summarized data of Table XV, however, show, that high selectivity between these positions is maintained. Very recently Moodie, Schofield, and Weston (64) themselves have extended their studies to the nitration of pseudocumene (1,2,4-trimethylbenzene) where formation of both the 5- and 6-nitro isomers clearly should be encounter controlled. As the reaction, however, maintained positional selectivity, they concluded that on the path of aromatic substitution, indeed two separate intermediates must be involved. One is obviously of benzenium ion nature, with the other preceding it. The nature of the latter was not discussed, but was termed only as the encounter pair.

$$\mathrm{ArH} + \mathrm{NO_2}^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{encounter pair}}{\text{e.p.}} \xrightarrow{\Sigma k_2} \underset{\text{Wheland intermediate}}{\mathrm{AHNO_2}^+}$$

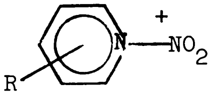
An intermediate, i.e., energy minimum on the potential energy profile of a reaction, however, clearly must have defined chemical bonding nature. In my view thus this picture seems to be very similar to the one we suggested in our work.

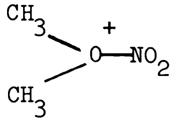
Concerning the nature of the nitrating agent, it is now clear that the nitronium ion is not the only possible nitrating agent. The nitrating ability of protonated acetyl and benzoyl nitrate, for example, is well established (59). Other nitrating agents,

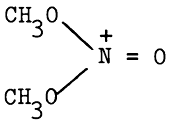
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

such as the N- and O- nitroxonium ion type transfer nitrating agents and the dimethyl nitracidium ion were already discussed.







The proton elimination step from the arenium ion intermediates to product is generally fast.

The proton elimination step from the nitroarenium ion intermediates of aromatic nitration was first studied by Melander in 1950, who found no kinetic isotope effect when comparing tritiated benzene with light-benzene (60). Similar studies since have shown this to be fairly general in aromatic nitractions (61). In our studies with deuteriated benzene, we found a small secondary inverse kinetic isotope effect (hexadeutero benzene reacting slightly faster than benzene $k_H/k_D = 0.84$) which can be considered in good accord with the rate determining initial π-complex formation. However, as shown by Myhre (62), when steric crowding increases the energy requirement for the proton-elimination step, aromatic nitrations in suitable crowded systems can, indeed, show substantial kinetic hydrogen isotope effects.

High Substrate High Postitional Selectivity

Not only the electrophilicity of the reagent, but also the nucleophilicity of the aromatic substrate can affect the selectivity of the nitration. This relates to both positional and substrate selectivities. Whereas in nitration selectivity is not much varied by changing the reactivity of the nitrating agent, selectivity of the reactions can be substantially changed by suitable deactivating substituents in the aromatics, which cause the relative height of the barrier to σ-complex formation to increase significantly, and thus cause the σ-type transition states to become of highest energy. This is well demonstrated in comparing nitration of nitrobenzene and nitrotoluenes (65). High substrate and positional selectivity (with preference for para nitration relative to the methyl group) indicates the σ-pattern of the reactions.

Whereas nitration of benzene and toluene with nitronium salts is generally too fast to allow noncompetitive rate measurement, in the case of nitrobenzene and nitrotoluenes, it is possible to carry out noncompetitive rate studies.

We have measured the rate of nitration of nitrobenzene, m-dinitrobenzene, and dinitrotoluenes by conventional methods. The rate data obtained were shown in Tables XVIII and XIX. For comparison, both relative reactivity values calculated from the separate rate determinations and those from competitive reactions are also shown in these tables, indicating that the relative reactivity

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Table XVII Competitive Nitration of Nitrobenzene and Nitrotoluenes with $NO_2^+PF_6^-$

	Relative rate		% dinitrotoluene					
	CH_3NO_2	96% H_2SO_4	2,3-	2,4-	2,5-	2,6-	3,4-	3,5-
Nitrobenzene	1	1	o:m:p in CH_3NO_2 = 10:88.5:1.5; in 96% H_2SO_4 = 7.1:91.5:7.4					
o-Nitrotoluene	384	545	57.4 71.2		1.7	40.9 28.8		
m-Nitrotoluene	91	138	42 28.4		18.6 9.9		35.8 60.1	3.6 1.6
p-Nitrotoluene	147	217		99.8 99.8			0.2 0.2	

Table XVIII. Rate of Nitration of Nitrobenzene and Nitrotoluenes with NO_2BF_4 in Nitromethane and Sulfuric Acid at 25°

ArH	NO_2BF_4, *M*	ArH, *M*	k_2, M^{-1} sec^{-1}	$k_{2(ArH)}/k_{2(NB)}$
		In CH_3NO_2		
Nitrobenzene	0.1–0.2	0.01–0.02	1.19×10^{-2}	1
o-Nitrotoluene	0.1–0.2	0.01–0.02	4.25	357 (384)[a]
m-Nitrotoluene	0.1–0.2	0.01–0.02	1.23	103 (91)[a]
p-Nitrotoluene	0.1–0.2	0.01–0.02	1.54	129 (147)[a]
		In 96% H_2SO_4		
Nitrobenzene	0.1–0.2	0.01–0.02	2.30×10^{-3}	1
o-Nitrotoluene	0.1–0.2	0.01–0.02	1.41	614 (545)[a]
m-Nitrotoluene	0.1–0.2	0.01–0.02	3.71×10^{-1}	161 (138)[a]
p-Nitrotoluene	0.1–0.2	0.01–0.02	5.22×10^{-1}	227 (217)[a]

[a] Data in parentheses are from competitive experiments.

Table XIX. Rate of Nitration of *m*-Dinitrobenzene and Dinitrotoluenes in Fluorosulfonic Acid at 95°

ArH	NO_2BF_4, *M*	ArH, *M*	k_2, M^{-1} min^{-1}	$k_{2(ArH)}/k_{2(mNB)}$
m-Dinitrobenzene	3.0–3.4	0.30–0.35	1.51×10^{-5}	1.0
2,4-Dinitrotoluene	2.0–2.5	0.20–0.30	1.19×10^{-2}	7.87×10^{2} (469)[a]
2,6-Dinitrotoluene	2.0–2.5	0.20–0.30	3.41×10^{-2}	2.25×10^{3} (2705)[a]

[a] Data in parentheses are from competitive experiments.

values obtained from the competitive method are, within the limit of the experimental error, quite consistent with those obtained from noncompetitive rate measurements.

Data of these studies indicate that there is substantial difference between the mononitration of toluene and benzene from the corresponding di- and trinitrations. Mononitration, as studied extensively, shows low substrate selectivity (k_T/k_B ranging from 27 to 15), and nitration of toluene generally shows high ortho/para isomer rate ratios, frequently exceeding 2. The amount of meta isomer is always low, ranging from 2 to 5%.

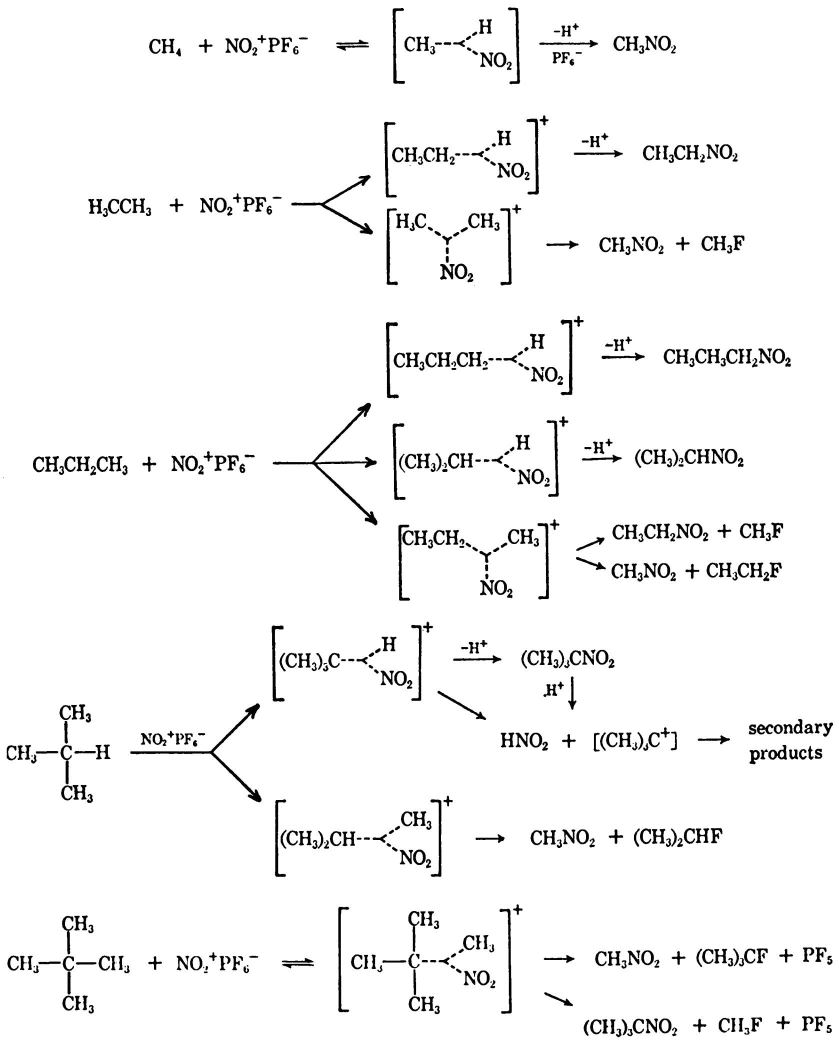
Because it is difficult to significantly change the nature of the electrophilic nitrating agent (no weakly electrophilic, highly selective nitrating agent was reported so far), all reported exothermic nitrations of toluene and benzene must be assumed to have transition states lying early on the reaction coordinate. In order to shift the transition state of highest energy to a "late" one resembling arenium ions, decrease of the nucleophilicity of the aromatic ring is, however, highly efficient. Nitrations of nitrobenzene (dinitrobenzene) and nitrotoluenes (dinitrotoluenes) show characteristics similar to those observed in other electrophilic reactions with σ-type transition states (i.e., high k_{CH3}/k_H rate ratios and preference of para over ortho substitution).

Due to the substantial difference in the nature of the nitration of benzene and toluene from that of nitration (dinitration) of nitrobenzene (nitrotoluenes) no direct comparison of these nitrations can be made. Rate differences of nitration of benzene and nitrobenzene can be estimated to be of the order of at least 10^6. Nitration of nitro(dinitro)benzene and nitrotoluenes shows high positional and substrate selectivity, indicating "late," i.e., benzenium ion like nature of the transition states. This is also reflected in the increasingly predominant para orientation (in relation to the methyl group) in the nitration of nitrotoluenes. This observation is significantly different from the generally high ortho/para nitrotoluene isomer ratios observed in the nitration of toluene. Thus the differing nature of nitration of toluene and nitrotoluenes was demonstrated. Care must be thus exercised in mechanistic considerations when attempting to compare nitration of aromatics of widely varying electron donor nature, such as benzene and toluene with nitro(dinitro) benzene and nitrotoluenes.

Aliphatic Nitration. Concerning mechanistic aspects of the nitronium ion nitration (and nitrolysis) of alkanes and cycloalkanes, experimental data indicate that they proceed in accordance with the generalized concept of electrophilic reactions (66) of single bonds involving two-electron three-center bonded transition states, formed by the nitronium ion attacking the covalent σ-bonds forcing them into electron-pair sharing. Whereas reaction of the C-H bond results in substitution of hydrogen for the nitro group,

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

reaction on C-C bonds causes nitrolysis as shown, for example, in the reactions of ethane, propane, isobutane, and neopentane (22).

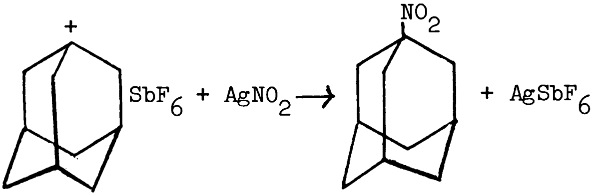


Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Tertiary C-H bonds show the highest reactivity. C-C bonds are generally more reactive than secondary or primary C-H bonds, leading to preferential nitrolysis of n-alkanes(cleavage nitration) The nitronium ion, which is linear itself, does not seem to exercise excessive steric hindrance in the transition states of the reactions, where it is substantially bent (indicated also from its behavior in electrophilic aromatic substitutions). Side products of the nitrolysis are methyl, ethyl, and isopropyl fluoride (formed by the reaction of PF_6^- with the cleaved alkylcarbenium ions) or secondary alkylation products, themselves capable of undergoing reaction with the nitronium salt.

Frontside attack by the electrophile, as suggested, should result in retention of optical activity, if reaction was carried out on an optically active hydrocarbon. Our studies in this regard are not yet completed. We have, however, been able to carry out NO_2^+ nitration of rigid systems, like adamantane.

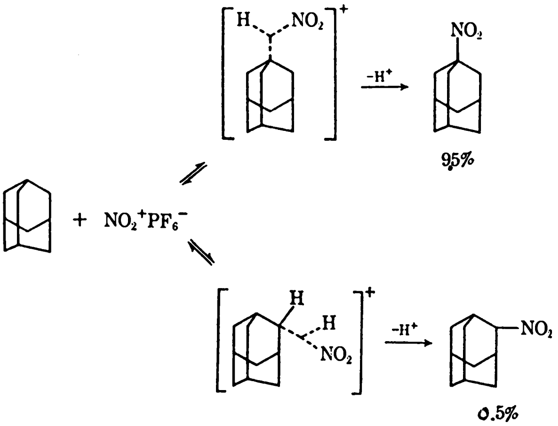
Adamantane is nitrated with nitronium salts in methylene chloride-sulfolane mixture, to give about a 10% yield of 1-nitroadamantane with a small amount of 2-nitroadamantane also formed (in less than 1% yield). As in the rigid cage compound the nitronium ion can't approach from the back-side, the geometrical restriction in the system clearly indicates that attack must be from the front-side. The reaction thus is an S_E2 like electrophilic substitution involving the σ-electron pairs of the involved CH-bonds. Alternatively, 1-nitroadamantane can also be prepared by an S_N1-type reaction, reacting the stable bridgehead adamantyl cation with nitrite ion.



The ease and predominant formation of the tertiary bridgehead 1-nitroadamantane in the electrophilic nitration of the rigid cage hydrocarbon clearly indicates the suggested mechanism since no "backside" attack is possible through the cage compound.

Contrasted with electrophilic aromatic nitration, electrophilic aliphatic nitrations are much affected by protolytic denitrations, which particularly with tertiary and secondary nitro compounds are of major importance. The fact that denitration affects electrophilic aliphatic nitration can be best demonstrated in the case of 2-nitro-2-methylpropane which was found to undergo protolytic cleavage in FSO_3H-SbF_5, $HF-SbF_5$, and also in $HF-PF_5$ solution even at -80°. The protolytic cleavage reaction yields tert-butyl cation and nitrous acid (or subsequently, nitrosonium ion). No nitronium ion is formed, as indicated by absence of any

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001



aromatic nitration product found when tert-$C_4N_9NO_2$ was treated with benzene and toluene in the presence of strong acids; only tert-butylated products were obtained.

$$(CH_3)_3CNO_2 \overset{H^+}{\rightleftharpoons} (CH_3)_3CNO_2H^+ \longrightarrow (CH_3)_3C^+ + HNO_2$$

The yields of electrophilic nitration of alkanes in solvents such as methylene chloride-sulfolane, are low.

The σ-basicity of alkanes obviously is lower than the *n*-basicity of lone-pair donor molecules used as solvent systems. This represents a major difficulty in achieving practical aliphatic nitrations with nitronium ions.

Also, the nitro products, being *n*-donors themselves, tend to slow down nitrations by complexing NO_2^+ and only low yields of nitroalkanes could be so far obtained, at least under the very mild reaction conditions used.

At 25°, 0.1% of nitromethane was obtained in the nitration of methane. Substantially (at least tenfold) increased yields are, however, obtained in HF and HSO_3F (or other superacid) solutions as solvent (see subsequent discussion). Higher alkanes and isoalkanes gave yields of 2-5% and adamantane was nitrated in 10% yield.

Whereas our studies centered so far primarily on the feasibility of the nitration of alkanes (cycloalkanes) with nitronium salts in aprotic solvent systems, once reactions are demonstrated they can, of course, also be carried out under more conventional conditions. Mixed acid (HNO_3-H_2SO_4) nitration of isobutane at 50° gave about 10% nitroproducts, with the relative ratio of CH_3NO_2, 28%;

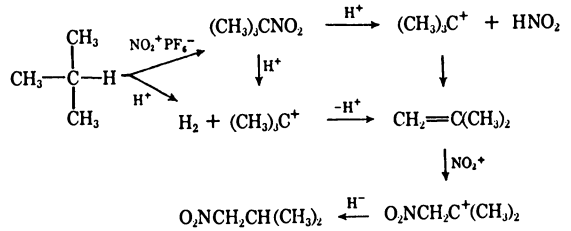
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

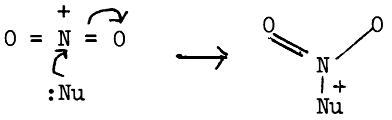
$CH_3CH_2NO_2$, 4.9%; $(CH_3)_2CHNO_2$, 0.5%; $(CH_3)_3CNO_2$, 66.6%. Mixed acid nitration can be complicated by protolytic cleavage of product nitroalkanes, by isomerization of the hydrocarbon oxidative side reactions, and, if higher reaction temperatures are applied, by free-radical nitration products. Nitroethane and 2-nitropropane formed in small amounts in the mixed acid nitration of isobutane can result from nitration of propane, formed *via* subsequent hydride transfer in the nitrolysis yielding nitromethane. In principle, however, there seems to be no reason why electrophilic aliphatic nitration should not become a general reaction, with a variety of nitrating agents capable to act as precursors to the nitronium ion.

The ease of protolysis of tertiary (and to a lesser degree secondary) aliphatic nitro compounds explains in part the complex reaction mixtures obtained in mixed acid nitrations of alkanes.

Anhydrous hydrogen fluoride and fluorosulfuric acid were found as improved solvents for the nitration of methane with nitronium salts. In these strong acid solvents even under the mild reaction conditions (room temperature) at least tenfold increased yields ($\sim$ 1%) could be obtained. As no protolytic reactions of methane take place in HF under the reaction conditions, side reactions are not observed. This is not the case in the nitration of isobutane in HF solution, where 90% of the nitroalkanes obtained consisted of 1-nitro-2-methylpropane. Since only traces of this isomer were found in nitronium salt nitration in aprotic CH_2Cl_2-sulfolane solution, the formation of 1-nitro-2-methylpropane must be considered due to formation of isobutylene (either from isobutane itself in HF containing PF_5 or more probably from the protolytic cleavage of 2-nitro-2-methylpropane).

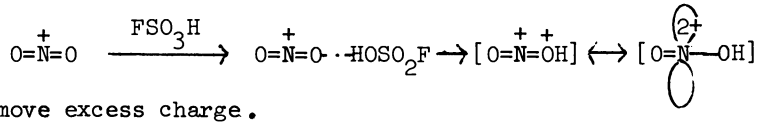


Concerning the nitrating ability of the nitronium ion, it should be realized that the linear nitronium ion is only a polarizable electrophile. NO_2^+ itself has no empty atomic or bonding molecular orbital available for interaction with the nucleophile. With the suitable electron donor (*i.e.*, π- or *n*-donor) substrates the reaction can be depicted in the following. The positive charge of the nitronium ion helps to bring NO_2^+ into proximity of the nucleophile, which then through interaction of its electron-pair will polarize the NO π-bond, and allow the reaction to proceed.



It is significant to note, however, that with highly deactivated substrates, such as for example m-dinitrobenzene, nitration with nitronium salts is not taking place with any appreciable rate in aprotic solvent media (65). On the other hand, when using protic solvents, such as fluorosulfuric acid, the nitronium ion in the strongly acidic media can with ease trinitrate benzene (12,65). Similar observations were made in nitration of alkanes (22).

In strictly aprotic media nitronium salts (such as $NO_2^+BF_4^-$ or $NO_2^+PF_6^-$) show no (or minimal) reactivity towards methane. However, in fluorosulfuric acid or HF-BF solution nitration takes place giving nitromethane. The reason for needed superacidic solvents seems to be to protosolvate the nitronium ion (67). The protonitronium ion (NO_2H^{2+}) if completely formed, would be a dicationic, unstable and consequently highly reactive species. Simonetta, indeed, calculated this dication, and found no energy minimum comparable to the nitronium ion in the gas phase dications are generally more unfavorable, due to the charge-charge repulsion, than in the condensed state, where solvation can help to remove excess charge.



$$\overset{+}{O=N=O} \xrightarrow{FSO_3H} \overset{+}{O=N=O}\cdots HOSO_2F \rightarrow [\overset{+\ +}{O=N=OH}] \longleftrightarrow [O=\overset{2+}{N}-OH]$$

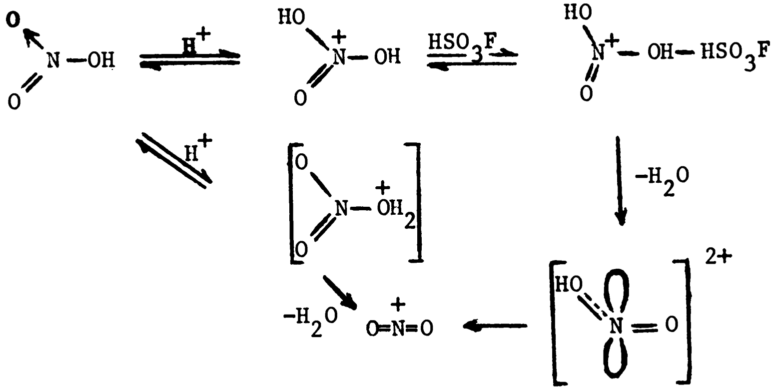
Indication for hydrogen bonding of the nitronium ion with fluorosulfuric acid can be seen from ir spectra in arsenic trifluoride solution (a suitable solvent for these studies). The HO stretching frequency of the acid in AsF_3 is shifted from about 3300 cm^{-1} to 3265 cm^{-1} upon addition of about 10% $NO_2^+PF_6^-$ to the system, with simultaneous broadening. At the same time the N-O stretching frequency at 2380 cm^{-1} remains practically unchanged, indicating no change in the force constant for the NO bond.

In mixed acid and related acidic solutions the formation of the nitronium ion can, indeed, be considered to proceed through a dicationic protosolvated species, which in the absence of a suitable nucleophile deprotonates to the more stable nitronium ion.

Ridd's recent observation of a medium effect on the nitronium ion in the nitric acid-acetic anhydride system indicating NO_2^+(HO Ac) as the possible nitrating agent is also of interest to be mentioned, (68), but of course CH_3CO_2H is more nucleophilic than FSO_3H.

It should be emphasized that the stability of intermediates and their reactivity are not parallel, but opposing properties. It was previously assumed, according to Ingold, that the existence

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001



of a reactive intermediate is convincingly established only if it can be directly observed or even isolated (such as the nitronium ion). With stable, isolable intermediates the question must be raised, however, whether these are, indeed, the reactive forms involved in reactions in solution. Nitronium salts themselves may be only of relatively limited electrophilic reactivity as polarizable reagents. They still will readily react with relatively strong electron donors such as n and π-donors which can polarize and eventually displace a bonding π-electron pair unto oxygen, but apparently are not capable of reacting with pure σ-donors, such as methane. In the latter case, it is suggested that protosolvated highly reactive species are the de facto reagents.

Gas Phase Molecule-Ion Nitration. Finally, for comparison with electrophilic nitration in solution, we also carried out in cooperation with Robert Dunbar and Jacob Shen studies of electrophilic molecule-ion nitrations in the gas phase using ion cyclotron resonance spectroscopy (69). The nitronium ion in the gas-phase itself does not give nitrated products, as first shown by Bursey (70). Instead, the following reaction takes place

$$C_6H_6 + \overset{+}{NO_2} \longrightarrow C_6H_6O^{+\cdot} + NO$$

indicating that in the gas-phase the linear nitronium ion interacts with the aromatic substrate through its oxygen, and not nitrogen pole giving the phenoxy radical ion. When using, however, a suitable nitrating agent, such as methylene nitrate which in the molecule-ion nitration reaction gives formaldehyde as the neutral leaving product taking away excess kinetic energy, electrophilic nitrations in the gas-phase could be studied.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

$$CH_2ONO_2^+ + ArH \longrightarrow ArNO_2^+ + CH_2O$$

Rather than attempting absolute rate determinations, the rates of the reactions were determined relative to the rates of benzene by competition experiments. The $CH_2ONO_2^+$ reactant ion was generated by electron bombardment at 14 eV from ethyl nitrate and was allowed to react competitively at about 5×10^{-5} Torr with a mixture of two aromatic species, with the relative peak heights of the two possible product ions (corrected for mass discrimination) giving the relative reaction rates for two aromatic substrates. In contrast to the analogous competition techniques in solution, no uncertainties can arise from the incomplete mixing since mixing is rapid and depletion of the neutral reactants is negligible, so that the relative intensities of the product ions should be a true measure of the relative reaction rates.

Bursey, has investigated the ionic reactions of benzene with ethyl nitrate at an ionizing voltage of 30 eV. We found that at 14 eV only three primary ions are formed with significant abundance, NO_2^+ and $CH_2\text{-}ONO_2^+$ from ethyl nitrate, and $C_6H_6^+$ from benzene. The only significant secondary ions formed are $C_2H_5\text{-}ONO_2$, NO_2^+(m/e 136), $C_6H_6O^+$(m/e 94), and $C_6H_6NO_2^+$(m/e 108). In agreement with Bursey, we find by ion cyclotron double resonance that $C_6H_6O^+$ has NO_2^+ as its precursor. Therefore, the only ion arising from reaction of benzene with $CH_2ONO_2^+$ is $C_6H_6NO_2^+$. This reaction was confirmed by double resonance. This was found to be true for all aromatic substrates investigated: attack on the aromatic molecule by $CH_2ONO_3^+$ either is followed by nitration or gave no product at all. The aromatic parent cations were also shown by double resonance not to yield significant $ArHNO_2^+$.

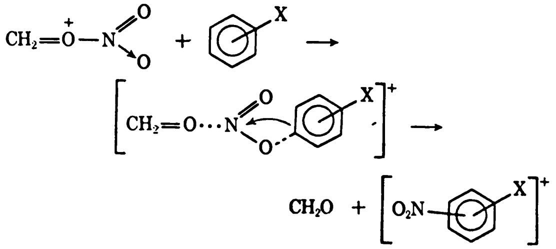
Table XX summarizes the obtained relative rates for gas-phase nitration of substituted benzenes and heteroaromatic compounds:

Table XX. Gas-Phase Molecule-Ion Nitration of Aromatics with $CH_2ONO_2^+$

Aromatic substrate	RelRate
Benzene	1.0
Benzene-d_6	1.0
Aniline	0
Anisole	0
Nitrobenzene	10
Pyrrole	0
Ethylbenzene	0
Toluene	0.3
Cyclopropylbenzene	0
Chlorobenzene	0.25
α,α,α-Trifluorotoluene	0.3
Pyridine	0.3
Fluorobenzene	0.55
Xylene (*o*, *m*, or *p*)	0
o-Difluorobenzene	0.25
m-Difluorobenzene	0.3
p-Difluorobenzene	0
Pentafluorobenzene	0
p-Bromoanisole	0
1,3,4-Trimethoxybenzene	0

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

There is an inverse correlation between the gas-phase relative rates of nitration and the generally observed trend of the relative rates of electrophilic aromatic substitutions in solution. Toluene reacts 3 times slower and nitrobenzene 10 times faster than benzene. This suggests that nitration in the gas-phase is nucleophilic in character, and thus does not correspond at all to solution-phase electrophilic nitration by the NO_2^+ ion. We tentatively suggest as a possible rationalization of this unexpected result that the gas-phase reaction involves primary electrostatic interaction of the aromatic substrate with the nucleophilic terminal oxygen of the $CH_2ONO_2^+$ cation, followed by displacement by the aromatic ring on nitrogen, with simultaneous elimination of formaldehyde.



Summary and Future Outlook

I have reviewed some of the research of my group in recent years involving aromatic and aliphatic nitration. Both preparative aspects as well as mechanistic studies directed to a better understanding of the nature of electrophilic nitration were discussed.

Concerning the future, I feel some of the areas of nitration which will be of significance are:

(1) Improved methods of nitration, emphasizing conditions to drastically reduce environmental pollution. Solid acid catalysts in connection with modified nitration systems will gain importance.

(2) Development of more selective nitration methods.

(3) Non-competitive rate studies of nitration of toluene and benzene with NO_2^+ salts. This is a particularly challenging problem as the reactions cannot be measured with the unusual fast kinetic methods based on equilibrium systems.

Acknowledgment

Support of our work by the U.S. Army Office of Research is gratefully acknowledged.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

Literature Cited

1. For reviews see (a) de la Mare, P.B.D. and Ridd, J.H., "Aromatic Substitution, Nitration and Halogenation", Butterworth (1959); (b) Olah, G.A. and Kuhn, S.J., in "Friedel-Crafts and Related Reactions.", Vol. III, p. 1393-1491, Wiley-Interscience, New York (1964); (c) Hoggett, J.G., Moodie, R.B., Penton, J.R. and Schofield, K., "Nitration and Aromatic Reactivity", Cambridge University Press, (1971).
2. (a) Ingold, C.K., Hughes, E.D., et al., J. Chem. Soc., (1950) 2400; (b) For a review see Ingold, C.K., "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press (1969).
3. Hantsch, A., Chem. Ber., (1925) 58, 941; Z. Phys. Chem., (1932) 149, 161.
4. (a) Olah, G.A. and Kuhn, S.J., Chem. Ind., (1956) 98, (b) Olah, G.A., Kuhn, S.J. and Mlinko, A., J. Chem. Soc. (1956) 4257.
5. Kuhn, S.J. and Olah, G.A., J. Amer. Chem. Soc., (1961) 83, 4564.
6. Giaccio, L.L. and Marcus, R.A., J. Amer. Chem. Soc. (1963) 84, 1838.
7. Radcliffe, L.G. and Pollitt, A.A., J. Soc. Chem. Ind. (1921) 40, 45T, 90T.
8. Drummond, A.A., J. Soc. Chem. Ind. (1922), 41, 338T.
9. Desvergnes, L., Chim. et Ind. (1931) 25, 291.
10. For example: Clarke, H.T., and Hartman, W.W., "Organic Syntheses", Coll. Vol. II, John Wiley and Sons, Inc., New York (1943) p. 526.
11. Olah, G.A. and Lin, H.C., J. Amer. Chem. Soc., (1974), 96, 549.
12. Olah, G.A. and Lin, H.C., Synthesis, (1974) 494.
13. Lin, H.C., Ph.D. Thesis, Case Western Reserve University (1972).
14. Olah, G.A., Nojima, M. and Kerekes, I., Synthesis (1973) 779.
15. Olah, G.A. Quinn, H.W. and Kuhn, S.J., J. Amer. Che. Soc., (1960) 82, 426.
16. Beilstein F., and Kurbatov, A., Ber. (1880), 13, 1818, 2029.
17. Konovalov, M., ibid, (1893) 26, 878; (1895) 28, 1852.
18. Markovnikov, V., ibid, (1899), 32, 1441, 1445; (1900) 33, 1905; (1902) 35, 1584.
19. Hass, H.B., et al., Ind. Eng. Chem. (1936) 28, 339; (1938) 30, 67; (1939) 31, 648; (1940) 32, 427; (1941) 33, 1138.
20. Grundmann, C., Chemie (1943) 56, 159.
21. For summaries on aliphatic nitration see (a) Asinger, F. "Parafins", Pergamon Press, New York, N.Y. (1968), Chapter 4, pp 365-482; (b) Topchiev, A.V., "Nitration of Hydrocarbons and Other Organic Compounds", Pergamon Press, New York, N.Y. (1960) (c) Titov, A.I., Tetrahedron (1963) 19, 557; (d) Kornblum, N., Org. React. (1962) 12, 101; (e) Larson, H.O. in "The Chemistry

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

of the Nitro and Nitroso Group", Vol. 1, H. Feuer, Ed., Wiley-Interscience, New York, N.Y. (1969), Chapter 6; (f) For a mechanism of gas-phase nitration, see Bachman, G.B. Addison, L.M., Hewett, J.V., Kohn, L. and Millikan, A., J. Org. Chem. (1952) 17, 906.
22. Olah, G.A. and Lin, H.C., J. Amer. Chem. Soc. (1971), 93, 1259.
23. Olah, G.A. and Lin, H.C., unpublished results.
24. Olah, G.A., Olah, J.A. and Overchuk, N.A., J. Org. Chem. (1965) 30, 3373.
25. Cupas, C.A. and Pearson R.L., J. Amer. Chem. Soc. (1968) 90, 4742; Pearson, R.L., Ph.D. Thesis, Case Western Reserve University (1971).
26. Olah, G.A., "Friedel-Crafts Chemistry", Wiley-Interscience, New York (1973).
27. Olah, G.A. and Kuhn, S.J. in "Friedel-Crafts and Related Reactions", ed. Olah, G.A., Vol. III, pp 1393-1491, Wiley-Interscience, New York, N.Y. (1964).
28. Price, C.C. and Scars, C.A., J. Amer. Chem. Soc. (1953) 75, 3276.
29. Kuhn S.J. and Olah, G.A., J. Amer. Chem. Soc. (1961) 83, 4564.
30. Dachlauer, K., Germ. Pat. 509,405 (1929) Chem. Abstr. (1931) 25, 781.
31. Hetherington, O., and Robinson, F.L., J. Chem. Soc. (1954) 3512.
32. Schaarschmidt, A., Ber. (1924) 57, 2065; Angew. Chem. (1926) 39, 1457.
33. Pinck, L.A., J. Amer. Chem. Soc. (1927) 49, 2536.
34. Titov, A.I. and Banyshnikova, A.N., J. Gen. Chem. (1936) 6, 1800; Titov, A.I., ibid (1937) 7, 667.
35. Goulden, J.D.S. and Millen, D.J., J. Chem. Soc. (1950) 2620; Millen, D.J., ibid., (1950) 2600.
36. Gillespie, R.J., Graham, J., Hughes, E.D., Ingold, C.K. and Peeling, E.R.A., ibid (1940) 2504.
37. Bachman, G.B., Feuer, H., Bluestein, B.R. and Vogt, C.M., J. Amer. Chem. Soc. (1955) 77, 6188; Bachman, G.B. and Vogt, C.M., ibid (1958) 80, 2987.
38. Evans, J.C., Rinn, H.W., Kuhn, S.J. and Olah, G.A., Inorg. Chem. (1964) 3, 857.
39. For an excellent summary, see De la Mare, P.B.D. and Ridd, J.H., "Aromatic Substitution, Nitration and Halogenation", Academic Press, Inc., New York, N.Y. (1959).
40. Klemenz, A. and Scholler, K., Z. anorg. Chem. (1924) 141, 231.
41. Millen, D.J., J. Chem. Soc. (1950), 2600.
42. Bachman, G.B. and Dever, J.L., J. Amer. Chem. Soc. (1958), 80, 5871.
43. Olah, G.A. and Lin, H.C., Synthesis, (1973) 488.
44. Olah, G.A. and Lin, H.C., J. Amer. Chem. Soc. (1974) 96, 2892

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

45. Olah, G.A., Kuhn, S.J. and Flood, S.H., ibid, (1961) 83, 4571.
46. Wibaut, J.P., Rec. Trav. Chim. (1915), 34, 291.
47. (a) Brown, H.C. and Nelson, K.L., J. Amer. Chem. Soc., (1953) 75, 6292; (b) Brown, H.C. and Smoot, C.R., ibid., (1956), 78, 6255.
48. Olah, G.A., Accounts Chem. Res. (1971) 4, 240 and references therein.
49. Olah, G.A. and Overchuk, N.A., Can. J. Chem. (1956) 43, 3279.
50. Tolgyesi, W.S., Can. J. Chem. (1965) 43, 343.
51. Christy, P.F., Ridd, J.H. and Stears, N.D., J. Chem. Soc., (B) (1970) 797.
52. Ritchie, C.D. and Win, H., J. Org. Chem. (1964) 29, 3093.
53. Olah, G.A., Kuhn, S.J. and Carlson, C.G., XIX, Int. Congress of Pure and Applied Chem., London (1963), Abstr. Papers. A. pp 1-81.
54. For the definition of carbocations, including differentiation of tetra- and pentacoordinated carbonium ions from trivalent carbenium ions, see Olah, G.A., J. Amer. Chem. Soc. (1972) 94, 808.
55. Olah, G.A., Kobayashi, S. and Tashiro, M., J. Amer. Chem. Soc. (1972) 94, 7448.
56. (a) Blackstock, D.J., Creteny, J.P, Fischer, A., Hartshorn, M.P., Richards, K.E., Vaughan, J. and Wright, G.J., Tetra. Letters (1970) 2793; (b) Perrin, C.L. and Skinner, G.A., J. Amer. Chem. Soc. (1971) 93, 3389; (c) Myhre, P.C., ibid., (1972) 94, 7921; (d) Kahn, R.C. and Groen, M.B., ibid., (1973) 95, 6128, Hahn, R.C. and Strack, D.L., ibid., (1972) 96, 4335; (e) Fischer, A. and Ramsay, J.N., J. Chem. Soc., Perkin Trans. (1973) 2237 and references therein.
57. (a) Olah, G.A., "Friedel-Crafts Chemistry", Wiley-Interscience, New York, N.Y. (1973) pp 30-31; (b) Olah, G.A. and Kuhn, S.J., J. Amer. Chem. Soc. (1964) 86, 1065 and references therein; (c) Myhre, P.C., Beug, M., Brown, K.S. and Ostman, B., J. Amer. Chem. Soc. (1971) 93, 3452; (d) Hahn, R.C., and Strack, D.L., J. Amer. Chem. Soc. (1974) 96, 4335.
58. Nightingale, D.V., Chem. Rev. (1947) 40, 117.
59. For a review, see ref. 1c, chapter 5, and references therein.
60. Melander, L., Arkiv. Kemi, (1950) 2, 211.
61. (a) Melander, L.C.S., "The Use of Nuclide in the Determination of Organic Reaction Mechanism", Reilly Lectures, Vol. XI, University of Notre Dame Press, Notre Dame, Ind. (1955; (b) Melander, L.C.S., "Isotope Effects on Reaction Rates", Ronald Press, New York, N.Y. (1960); (c) Zollinger, H., Experientia, (1956) 12, 165; Annu. Rev. Phys. Chem. (1962) 13, 400; (d) Zollinger, H., Advan. Phys. Org. Chem. (1964) 2, 163; (e) Berliner, E., Progr. Phys. Chem. (1964) 2, 253; (f) Cerfontain, H., Hofman, H.J. and Telder, A., Recl. Trav. Chim. Pays-Bas (1964) 83, 493; Olah, G.A., J. Tenn. Acad. Sci. (1965) 40, 77.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

62. Myhre, P.C., Beug, M. and James. L.L., J. Amer. Chem. Soc., (1968) 90, 2105.
63. Coombes, R.G., Moodie, R.B. and Schofield, K., J. Chem. Soc. (B)(1968) 800; (1969) 52.
64. Moodie, R.B., Schofield, K. and Weston, J.R., J. Chem. Soc., Comm. (1974) 382.
65. Olah, G.A. and Lin, H.C., J. Amer. Chem. Soc. (1974) 96, 549.
66. For a discussion see, Olah, G.A., "Carbocations and Electrophilic Reactions", Verlag-Chemie-Wiley, (1973).
67. Olah, G.A., Germain. A.,Lin, H.C., and Forsyth, D., J. Amer. Chem. Soc. 97, 2928 (1975)
68. Hartshorn, S.R., Hoggett, J.G., Moodie, R.B., Schofield, K., and Thompson, M.J., J. Chem. Soc. (B) (1971) 2461.
69. Dunbar, R.C., Shen, J., and Olah, G.A., J. Amer. Chem. Soc. (1972) 94, 6882.
70. Benezra, S.A., Hoffman, M.K. and Bursey, M.M., J. Amer. Chem. Soc. (1970) 92, 7501; Hoffman M.K. and Bursey, M.M., Tetrahedron Letters (1971) 2539.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch001

2

The Mechanism of Aromatic Nitration Reactions

LEON M. STOCK

Department of Chemistry, University of Chicago, Chicago, Ill. 60637

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Evidence developed in large measure by Ingold, Hughes, and their students provided strong support for the view that the nitration reactions of aromatic compounds proceeded via the nitronium ion under a variety of conditions including, for example, nitration by nitric acid in acetonitrile, nitration by nitric acid in acetic anhydride, and nitration by nitric acid in mixed acid.[1,2] Each new investigation of the reaction yielded additional evidence for this idea.

Mechanism I

$$\mathrm{HONO_2 + H^+ \rightleftharpoons H_2O + NO_2^+}$$

$$\mathrm{NO_2^+ + ArH \longrightarrow ArNO_2 + H^+}$$

Ingold and his associates used this reaction to establish the reactivity for a great variety of aromatic compounds.[1] They observed that the relative rates and isomer distributions were essentially independent of the conditions used in the nitration reaction. To illustrate, under the conditions of these various nitration reactions, chlorobenzene reacts less rapidly than benzene whereas toluene reacts more rapidly than benzene. Knowledge of the isomer distributions enables the calculation of the statistically corrected partial rate factors, $k_o/k_H = \underline{o}_f$, $k_m/k_H = \underline{m}_f$, and $k_p/k_H = \underline{p}_f$. Typical results are presented in Table I.

The same reactivity pattern for the activated toluene and the deactivated chlorobenzene is generally observed in electrophilic substitution reactions. Indeed, the results for nitration obey a linear free energy relationship based on σ^+ as shown in Figure 1.[4]

This relationship does not differ from the relationships for other electrophilic substitution reactions as shown for noncatalytic bromination and for the acid-catalyzed bromination reaction with hypobromous acid in aqueous dioxane in Figures 2 and 3.[5]

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

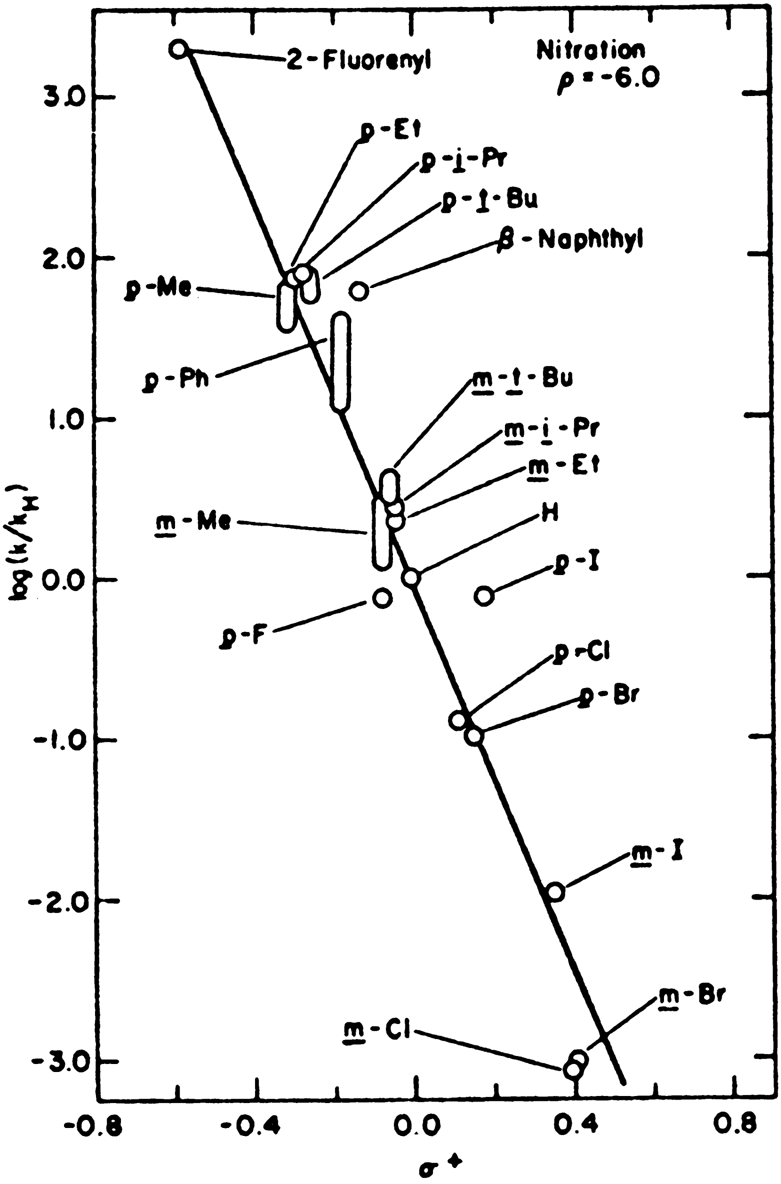
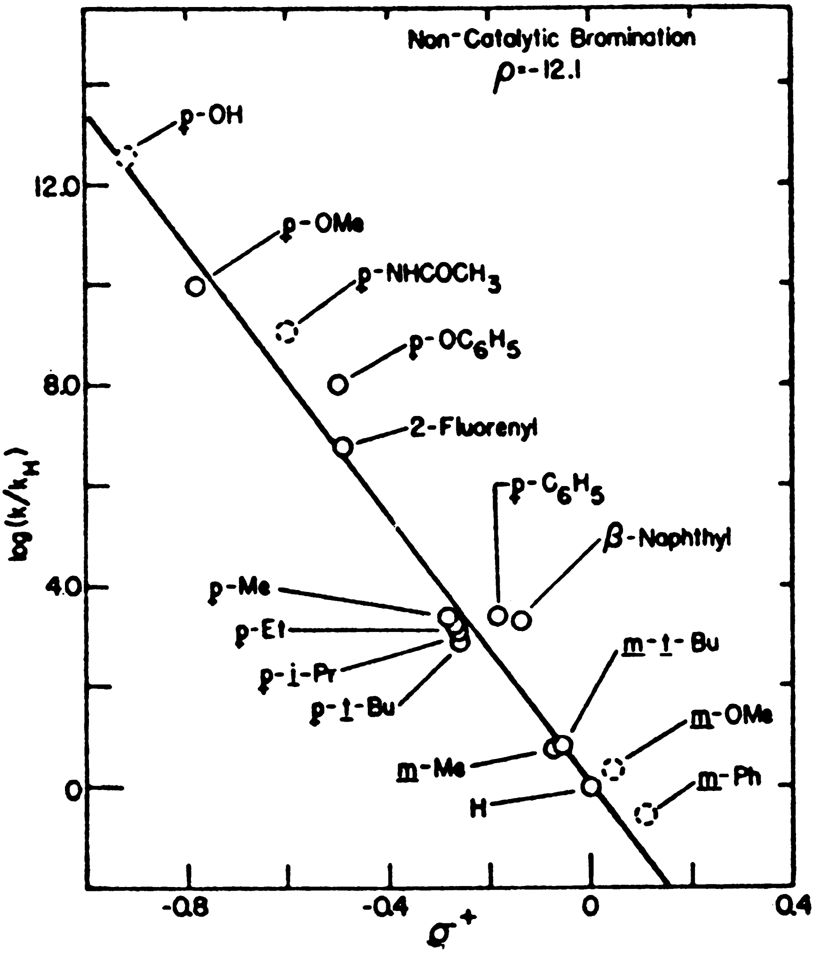


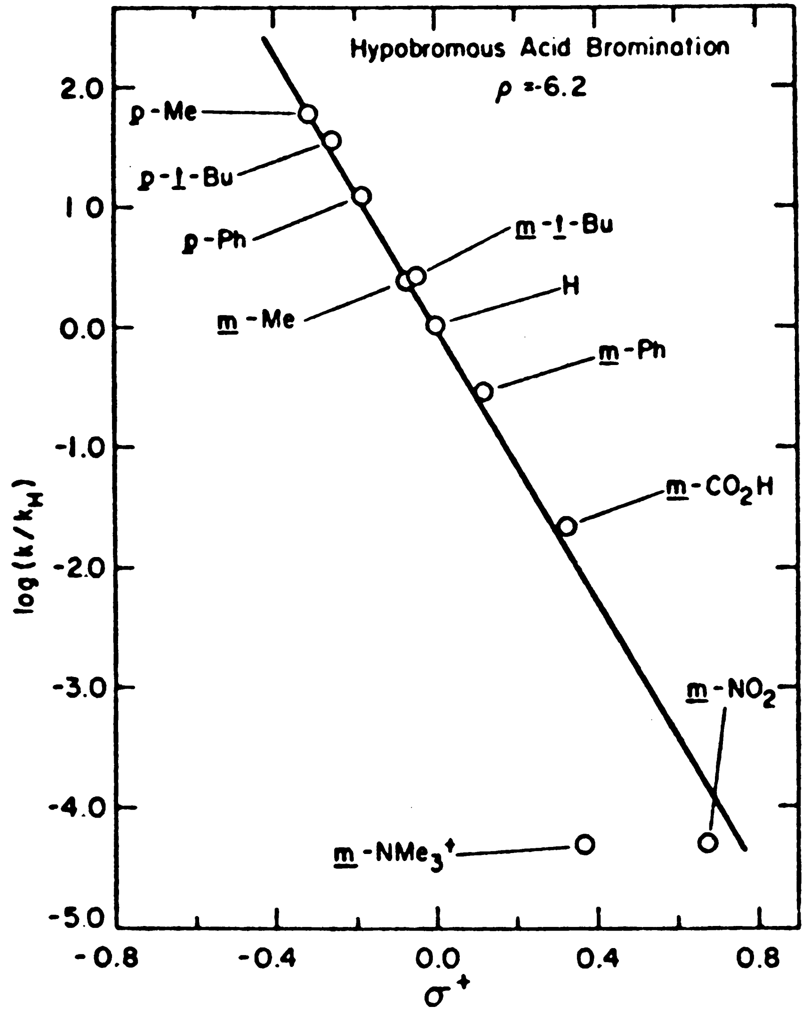
Figure 1. The relationship between the partial rate factors for nitration and σ^+

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002



Figures 2. The relationships between the partial rate factors for non-catalytic bromination and σ^+

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002



Figures 3. The relationships between the partial rate factors for hypobromous acid-catalyzed bromination and σ^+

Table I. Partial Rate Factors for the Nitration of Toluene and Chlorobenzene.[a]

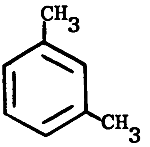
Compound	Relative Rate k/k_B	Isomer Distribution *o*-	*m*-	*p*-	Partial Rate Factor o_f	m_f	p_f
Toluene	21	61.7	1.9	36.4	38.9	1.3	45.8
Chlorobenzene	0.031	29.6	0.9	69.5	0.028	0.00084	0.130

[a] Nitric acid in nitromethane at 25°, Ref. 3.

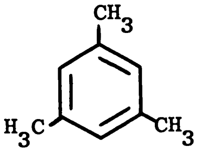
In summary, all the early kinetic and spectroscopic evidence support the contention that the nitronium ion is the effective electrophilic agent. Moreover, the rate data for the nitration reaction presented in Table I and illustrated in Figure 1 are representative of the normal reactivity pattern observed for many other electrophilic substitution reactions as shown by the results displayed in Figures 2 and 3.

Nitronium Salt Nitration-Mixing Control

In 1961, Olah, Kuhn, and Flood reported that the nitration reactions with nitronium salts such as nitronium tetrafluoroborate and hexafluorophosphate were quite anomalous.[6] When benzene and toluene were reacted competitively with these nitronium salts in sulfolane, analysis of the products revealed that toluene was only about 1.5-fold more reactive than benzene.[7] Indeed, neither *m*-xylene nor mesitylene were importantly more reactive than benzene under these conditions. The partial rate factors



$$\frac{k}{k_B} = 1.65$$



$$\frac{k}{k_B} = 2.71$$

calculated from these results are presented in Table II.[8]

Two immediate problems were recognized. First, all the prior work had led to the conclusion that the nitration reaction occurred via the nitronium ion. Yet, when the nitronium ion was

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Table II. Results for the Competitive Nitration of Toluene and Benzene with Nitronium Tetrafluoroborate in Sulfolane[a]

Compound	Relative Rate	Isomer Distribution			Partial Rate Factor		
	k/k_B	o-	m-	p-	o_f	m_f	p_f
Toluene	1.67	65.4	2.8	31.8	3.2	0.14	3.2
Chlorobenzene	0.14	22.1	0.7	76.6	0.093	0.002	0.64

[a] Ref. 6.

used as the reagent, quite different partial rate factors were obtained. Second, although the rate data for chlorobenzene are not anomalous, the reactivity pattern for toluene is distinctly abnormal with m_f^{Me} less than one and with the relative reactivity of the other more highly alkylated benzenes much less than expected.

Ingold, Lee, and Wei have discussed the conditions under which the competition method may not yield accurate relative rate data.[9-11] Lee in a careful analysis of the problem pointed out that the relative reactivities derived from competition experiments are invalid when significant reaction occurs before the reagents are adequately mixed. Tolgyesi examined this feature of the nitronium salt nitration reaction. He reported that the rate of mixing of the reagents influenced the proportions of nitrobenzene and nitrotoluene produced in the competitive nitration reactions with the nitronium salts.[12] Olah and Overchuck disputed these observations.[13] They argued that impurities in the solvent and reagents influenced Tolgyesi's observations.

The controversy between Tolgyesi and Olah was resolved by Ridd and his students in a study of the nitration of bibenzyl.[14-16] Bibenzyl was selected for study because the introduction of a nitro group into one ring has a negligible influence

$$C_6H_5CH_2CH_2C_6H_5 \rightarrow C_6H_5CH_2CH_2C_6H_4NO_2 \rightarrow O_2NC_6H_4CH_2CH_2C_6H_4NO_2$$

on the reactivity of the other ring, i.e. the influences of the $O_2NC_6H_4CH_2CH_2$- and $C_6H_5CH_2CH_2$- groups are not importantly different. Thus, a statistical product distribution is expected for the nitration reaction. Ridd tested this idea by the study of the nitration of excess bibenzyl with nitric acid in acetic anhydride.[16] The results shown in Table III reveal that the expected result was obtained. In sharp contrast, when the nitration reaction was carried out with nitronium tetrafluoroborate in sulfolane, a distinctly astatistical product distribution was obtained with a large excess of dinitrobenzyls, Table III.[14-16]

The change in the product distribution is dramatic. The high proportion of dinitrobibenzyls indicate that the mixing rate

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Table III. Reaction Products for the Nitration of Bibenzyl by Nitric Acid in Acetic Anhydride and by Nitronium Tetrafluoroborate in Sulfolane[a]

Product	Statistical Product Ratio	Observed Product Ratio			
		HNO_3 in Ac_2O[b]		NO_2BF_4 in $C_4H_8SO_2$[c]	
Bibenzyl	56.25	45.3			
2-Nitro	43.75	20.9	49.5	9.8	22.2
4-Nitro		28.6		12.4	
2,2'-Dinitro	6.25	1.1	5.1	14.8	77.8
2,4'-Dinitro		2.4		37.9	
4,4'-Dinitro		1.6		25.1	

[a] Ref. 14-16. [b] In a typical experiment 0.04 mole bibenzyl was reacted with 0.027 mole of nitric acid in acetic anhydride. [c] Several concentrations of the reagents were studied. These results are for bibenzyl = 0.25M and the nitronium salt 0.125M.

is comparable with the nitration rate for the reaction of nitronium salts with aromatic compounds in sulfolane, nitromethane, and apparently other organic solvents. As noted by Tolygesi, the simple competition method is inadequate for the definition of relative reactivity in aromatic nitration by nitronium salts. The partial rate factors derived from the competitive rate data are anomalous because the mixing rates dominate the chemistry. These data are, accordingly, meaningless for the analysis of reactivity patterns and for the definition of mechanisms.[2,16,17]

Nitric Acid Nitration-Encounter Control

Important new chemistry was obtained in 1968 by Coombes, Moodie, and Schofield and their associates at Exeter.[18] They first investigated the rates of nitration of simple aromatic compounds in aqueous sulfuric acid and aqueous perchloric acid.[18] When the reaction is carried out in 60-70% acid, with the aromatic compound at low concentration, about 10^{-4} M, the observed second order rate constant for the nitration of benzene is 5.8 x 10^{-2} l $mole^{-1}$ sec^{-1} (68.3% sulfuric acid) and 8.3 x 10^{-2} l $mole^{-1}$ sec^{-1} (61.1% perchloric acid). Individual experiments with nitric acid in excess indicate that the reaction is first-order in the concentration of the aromatic compound. Variations in the concentration of nitric acid established that the reaction was also first order in nitric acid. Further, they found that the second order rate constant for the nitration of benzene (about 10^{-4} M) by excess nitric acid increased as the acid strength of the reaction medium increased. The results are sketched in Figure 4.

The changes in the second-order rate constant for benzene parallel the anticipated change in the concentration of nitronium ion in the reaction media. It was concluded that the large rate variations for benzene reflected changes in the concentration of nitronium ion in the reaction solution.

$$\text{Rate} = k[\text{ArH}][\text{HNO}_3]\ a_{\text{H}^+}$$

Schofield and his associates pointed out, however, that the reaction between benzene and the nitronium ion must be a rather fast reaction because the concentration of the nitronium ion is only about 10^{-8} M in the aqueous acid solvents. Indeed, the value estimated for k_2 for benzene, about 10^6 l mole^{-1} sec^{-1}, is only about 100-fold less than the estimated rate constant for a diffusion controlled reaction in sulfuric acid.[18]

Extension of the investigation to other aromatic compounds provided equally interesting observations. The second-order rate constants for aromatic compounds which are less reactive than benzene were established by the study of the reaction in more acidic media.[19-21] The reaction rate data determined in this work are examined in Figure 5.

The reactivity pattern for aromatic compounds which are less reactive than benzene is entirely normal.[19-21] The ρ^+ value, about -6, is quite similar to the ρ^+ value obtained in earlier studies of the nitration reaction in organic solvents as shown in Figure 1. All these results are consistent with nitration by the same agent, the nitronium ion, in organic media as well as in aqueous acid.

The kinetic behavior of the aromatic compounds which are more reactive than benzene have also been examined with care.[18,19] As discussed, the observed second-order rate constants for the nitration of benzene require that the second-order rate constant for the reaction between nitronium ion and benzene approach the diffusion limit for 60-70% aqueous acid. The kinetic results for toluene obey the same rate law which was found to be applicable for benzene and the less reactive molecules. More recent work by Chapman and Strachan[22] using stopped flow techniques established that the nitration of toluene in aqueous acid proceeds by both first and second-order paths, Table IV.

The reaction is zero-order in toluene in the more concentrated acid but first-order in toluene in the less acidic solvents.

The rate data and the isomer distribution for the nitration of toluene under these conditions define the partial rate factors presented in Table V.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

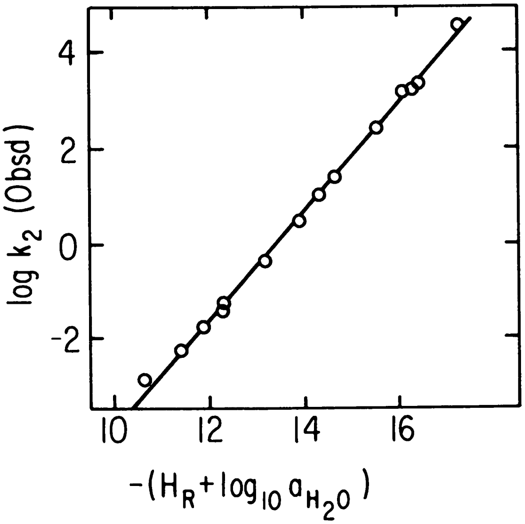


Figure 4. The relationship between the observed second-order rate constant for the nitration of benzene and the acidity function

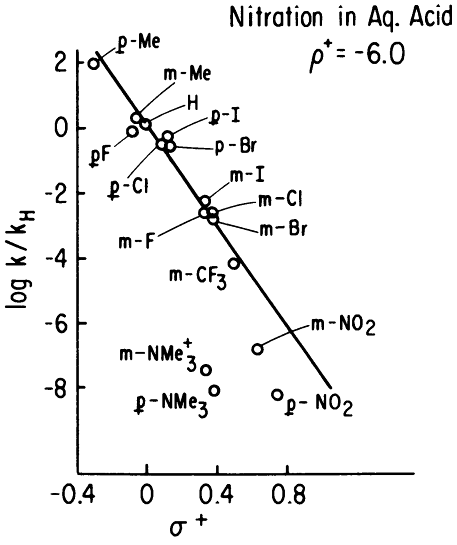


Figure 5. The relationship between the partial rate factors for nitration in aqueous sulfuric acid and σ⁺

Table IV. First and Second-Order Rate Constants for the Nitration of Toluene in Aqueous Sulfuric Acid at 25°.

Acidity, % H_2SO_4	Rate Constants k_1,[a] sec^{-1}	 k_2,[b] $l\ mole^{-1}\ sec^{-1}$
74.70	0.8	230 (170)[c]
77.00	1.8	1700 (1200)[c]
78.95	5.0	8300 (6600)[c]
80.10	6.4	-
81.45	8.3	-

[a] First-order in nitric acid. [b] First-order in nitric acid, first order in toluene. [c] Ref. 18.

Table V. Relative Rates and Partial Rate Factors for the Nitration of Toluene in 68.3% Sulfuric Acid[a]

	Isomer Distribution			Partial Rate Factors		
k_T/k_B	o-	m-	p-	o_f	m_f	p_f
17	60	3	37	31	1.5	38

[a] Ref. 23.

The partial rate factors estimated for these reaction conditions differ only modestly from the data shown in Table I for the nitration reaction in non-aqueous organic media.

For compounds which are more reactive than toluene, the second-order rate constants reach a limiting value. This feature of the reaction is illustrated by the results summarized in Table VI.

These results are typical for the nitration reaction under many conditions. The second-order rate constants for aromatic nitration reach a limiting value for nitric acid nitration in aqueous sulfolane, nitric acid nitration catalyzed by sulfuric acid in acetic acid, nitric acid nitration in aqueous perchloric acid, and nitric acid nitration in aqueous nitromethane.[23]

The simplest explanation which can accommodate all the facts is presented as Mechanism II.[2,18,22]

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Table VI. Relative Rate Constants for the Nitration of Aromatic Compounds in 68.3% Sulfuric Acid[a]

Compound	Relative Rate[b]
Benzene	1.00
Toluene	17
o-Xylene	38
p-Xylene	38
m-Xylene	38
Mesitylene	36

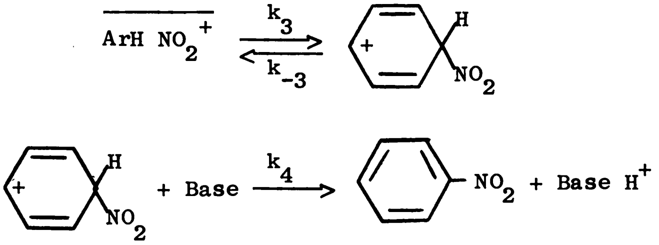
[a] Ref. 23. [b] The second-order rate constant for benzene is 5.8 x 10^{-2} 1 mole^{-1} sec^{-1}.

Mechanism II

$$HNO_3 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + NO_2^+$$

$$NO_2^+ + ArH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \overline{ArH\ NO_2}^{\,+}$$

Encounter Complex



Mechanism II is unusual only in the sense that an encounter complex is specifically considered as an intermediate.[24]

The nitration reaction does not, under these conditions, exhibit a primary kinetic isotope effect.[1,2] Consequently, the rate of formation of the benzenonium ion or one of the prior reactions must be the rate limiting process. The appropriate rate law based on steady state approximations for the nitronium ion and the encounter complex is readily derived.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

$$\text{Rate} = \frac{k_1 k_2 k_3 [\text{ArH}][\text{HNO}_3] a_{\text{H}^+}}{k_{-1}\, a_{\text{H}_2\text{O}} (k_3 + k_{-2}) + k_2 k_3 [\text{ArH}]}$$

Chapman and Strachan have shown that the nitration of toluene may be zero-order or first-order in the aromatic compound. The zero-order result corresponds to the rate determining formation of the nitronium ion.

$$\text{Rate} = k_{\text{obsd}} [\text{HNO}_3] a_{\text{H}^+}$$

This result is realized when the condition

$$k_2 k_3 [\text{ArH}] \gg k_{-1}\, a_{\text{H}_2\text{O}}\, (k_3 + k_{-2})$$

is satisfied. On the other hand, when the reaction occurs at the diffusion limit, as for the xylenes, mesitylene and other reactive compounds in aqueous sulfuric acid,[18,19,23] the rate law is

$$\text{Rate} = k_{\text{obsd}}\, [\text{ArH}][\text{HNO}_3] a_{\text{H}^+}$$

with a limiting value for k_{obsd}. The required condition is

$$k_{-1}\, a_{\text{H}_2\text{O}} \gg k_2 k_3 [\text{ArH}] \,/\, (k_3 + k_{-2}) \text{ with } k_3 \gg k_{-2}$$

and the formation of the encounter complex is the rate limiting step. Finally, the rate data for the nitration of toluene, benzene, and the other less reactive aromatic compounds obey a third rate law

$$\text{Rate} = k_{\text{obsd}}\, [\text{HNO}_3][\text{ArH}] a_{\text{H}^+}$$

with k_{obsd} dependent on the structure of the aromatic compound. For these cases, the required condition is

$$k_{-1}\, a_{\text{H}_2\text{O}} \gg k_2 k_3 [\text{ArH}]/(k_3 + k_{-2}) \text{ with } k_3 \ll k_{-2}$$

and the formation of the benzononium ion is the rate determining step.

In summary, the kinetic observations for aromatic nitration provide a consistent pattern of results. Conventional behavior is observed in the aqueous acid solvents for the compounds which are less reactive than the xylenes. However, the aromatic compounds which are approximately 50-fold more reactive than benzene exhibit a limiting reaction rate in these solvents. The rate limit can be identified with the diffusion controlled formation of the encounter complex.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Nitration in Organic Solvents

The nitration reactions of reactive compounds also approach a limiting rate in aqueous organic solvents. In these media, the nitration reaction is slower and the diffusion processes do not become kinetically important until the aromatic molecules are about a thousand-fold more reactive than benzene. In this case, the partial rate factors for the nitration of toluene are kinetically significant. However, the results for active molecules such as mesitylene are still complicated by diffusion rates.

Complex kinetic behavior is often observed and considerable effort is required to define the reaction path. Thus, Coombes in a recent investigation of the nitration reaction in carbon tetrachloride pointed out that the reaction with mesitylene approached the encounter controlled diffusion limit.[25] However, he noted that the work was incomplete.

Acetic anhydride has long been a popular solvent for the study of nitration.[1,2] In this medium nitric acid is converted to acetyl nitrate and acetic acid. Early interpretations of the rather complex kinetic data suggested that the nitronium ion was the effective agent.[1,2] Hartshorn and the Exeter group showed that the reaction of mesitylene was encounter controlled.[26] In a more recent study, Marziano, Rees, and Ridd found that the complex kinetic behavior results, at least in part, from the solvent effect of variations in the concentration of the hydrocarbon.[26] They conclude that caution is necessary in interpretation of the available data but note that several routes for the formation of nitronium ion solvated by acetic acid are compatible with the results.

Olah and Lin studied the boron trifluoride-catalyzed reaction of methyl nitrate with aromatic compounds in nitromethane.[28a] Using competition methods they found that the toluene to benzene rate ratio was 25 and that the rate ratios for the methylbenzenes, Table IX, reached a limiting value, about 1000. Unfortunately, kinetic rate data were not obtained. However, the leveled reactivity of the polymethylbenzenes suggests that these compounds react at the encounter controlled diffusion limit.

The reactivity pattern for nitration in organic solvents does not differ appreciably from the reactivity pattern for the reaction in highly acidic, perhaps aqueous, solvents. These results suggest that a common intermediate, presumably the nitronium ion, is involved in all these reactions.

Product Distributions

Aromatic nitration reactions exhibit, under all conditions, important intramolecular selectivity. The isomer distributions for the reactions of toluene under a variety of conditions, Table VII, illustrate this feature.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

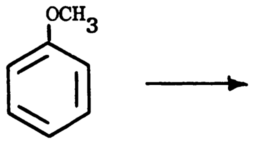
Table VII. Isomer Distributions in the Nitration of Toluene

Conditions	Isomer Distribution			Ref.
	o-	*m*-	*p*-	
$HNO_3, CH_3NO_2, 25^o$	61.5	3.1	35.4	29
$HNO_3, CF_3CO_2H, 25^o$	61.6	2.6	35.8	29
$AcONO_2, Ac_2O, 30^o$	58.1	3.7	38.2	29
$MeONO_2, BF_3, CH_3NO_2, 25^o$	63.9	3.4	32.7	28a
$NO_2BF_4, C_4H_8SO_2, 25^o$	65.4	2.8	31.8	29
$NO_2BF_4, CH_2Cl_2, -65^o$	56.6	0.6	42.8	30
$NO_2CF_3SO_3, CH_2Cl_2, -60^o$	62.1	0.5	37.4	30

[a] Heterogeneous.

At ambient temperatures, the nitration of toluene produces the *ortho* and *para* isomers dominantly with between 2 and 4% *meta* product. A similar product ratio is obtained when the reaction is carried out heterogeneously with mixed nitric and sulfuric acid. However, as expected, greater selectivity is achieved at low temperatures as shown by the reactions with nitronium salts.[30] The fact that the reaction yields virtually the same product distribution under all conditions supports the view that the same reagent, the nitronium ion, is the effective agent under all conditions.[1,2]

The nitration reactions also exhibit high selectivity when the reactions proceed at the encounter controlled diffusion limit. To illustrate, the nitration of anisole yields little *meta* product; the *ortho* and *para* isomers are produced almost exclusively.[19,28] Similarly, the substitution products of *m*-xylene



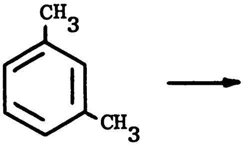
28% 2-Nitroanisole

<1% 3-Nitroanisole

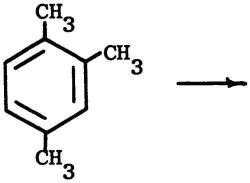
71% 4-Nitroanisole

are formed selectively with no detectable 5-nitro-1,3-dimethylbenzene.[29a] Moodie, Schofield, and Weston examined the diffusion limited nitration of pseudocumene in aqueous sulfuric acid.[31] In addition to the products of *ipso* substitution, they found that the 5-nitro isomer was formed in preference to the related 6-nitro product.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

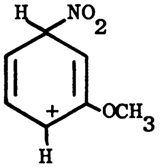


15%	2-Nitro-1,3-dimethylbenzene
85%	4-Nitro-1,3-dimethylbenzene

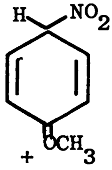


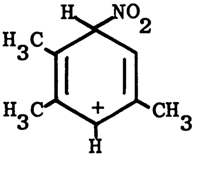
56%	Ipso Adducts
7%	3-Nitro-1,2,4-trimethylbenzene
33%	5-Nitro-1,2,4-trimethylbenzene
4%	6-Nitro-1,2,4-trimethylbenzene

In all these cases, the product distributions reflect the relative stability of the bezenonium ions.

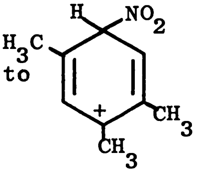


unstable compared to



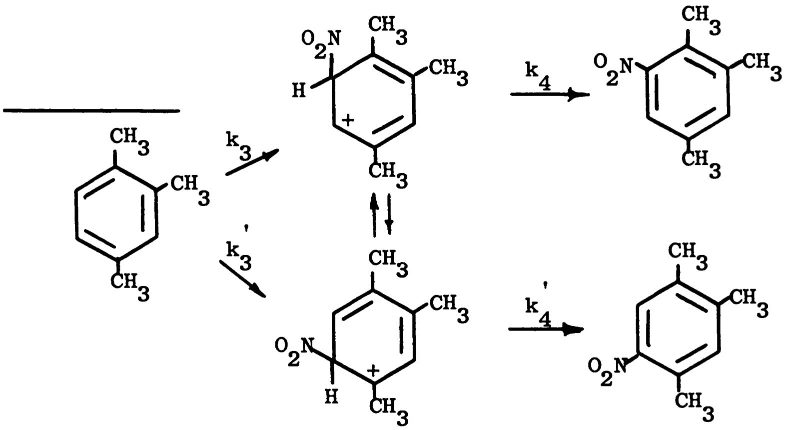


unstable compared to

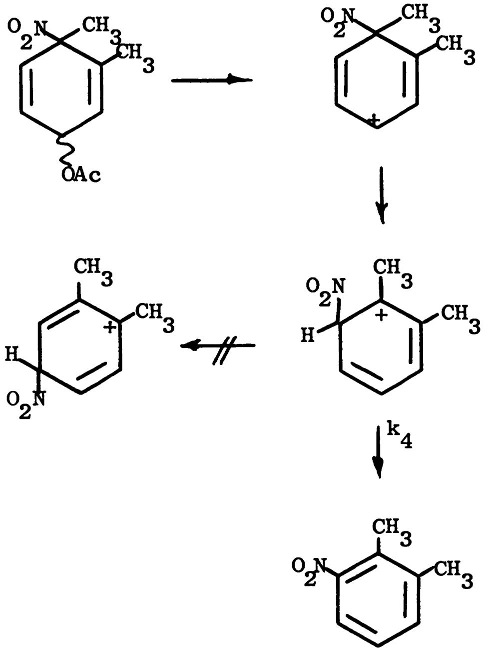


The product ratios can, in principle, be dictated by the relative rates of formation of the benzenonium ions, k_3, or by the equilibration of the ions as shown in Mechanism III.

Mechanism III



Direct evidence is not available in all cases. However, the solvolysis of 4-acetoxy-1-nitro-1,2-dimethylcyclohexa-2,5-diene leads to the exclusive formation of 3-nitro-1,2-dimethyl-



Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

benzene.[32] Further rearrangement to the 4-nitro derivative does not occur. Therefore, the rate of proton removal is apparently much greater than the rate of isomerization. Related adducts react in similar ways.[33] Consequently, it seems safe to conclude that the isomerization reactions of the benzenonium ions do not compete with the base-catalyzed proton abstraction reactions in the aqueous acids and that the energy requirements for the conversion of the encounter complexes to the benzenonium ions dictate the product distribution. Energy profiles compatible with the kinetic observations and with the product distributions are shown in Figure 6.

The energy requirements for the formation of certain benzenonium ions, e.g. those ions which are less stable than 1-nitrobenzenonium ion such as the halo derivatives and 3-methoxy-1-nitrobenzenonium ion and even the more stable 2-, 3-, and 4-methyl-1-nitrobenzenonium ions, are larger than the energy requirements for the diffusive dissociation of the encounter complex. These ions are, accordingly, produced in kinetically significant reactions as shown in Figure 6A. On the other hand, the energy requirements for the formation of other more stable benzenonium ions, e.g. the polymethylbenzene derivatives and the 2- and 4-methoxy-1-nitrobenzenonium ions, are less than the energy requirements for the dissociation of the encounter complex. Thus, the conversion of the encounter complex to the ion is not kinetically important as shown in Figure 6B. However, the study of the nitration of pseudocumene[31] reveals that the relative stabilities of the benzenonium ions determine the product distribution. Indeed, the activation energy difference for the conversion of the encounter complex to the 5- and 6-nitrobenzenonium ions is about 1.2 kcal mole.$^{-1}$ The activation energy for the conversion of the encounter pair to the benzenonium ion is not known. However, this energy barrier cannot exceed the low activation energy for the dissociation of the encounter pair. The structural characteristics remain important even though the energy barriers for the formation of the benzenonium ions are modest.[34] As yet no really unusual, intramolecular patterns of reactivity have emerged for nitration. Indeed, essentially the same product distributions are obtained when nitration occurs at the diffusion limit in aqueous acid solvents and when the reaction proceeds more slowly in organic solvents. Apparently, the differences in the energy barriers for the formation of the benzenonium ions in these solvent systems differ only modestly and the same factors govern the product distribution even though the rate determining steps are different.

The partial rate factors for nitration are compared with the related data for acetylation and chlorination in Table VIII.

As already discussed, the product distributions and the partial rate factors for nitration do not depend importantly on the character of the supplied reagent. A similar pattern of reactivity is observed for Friedel-Crafts acylation. In both re-

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

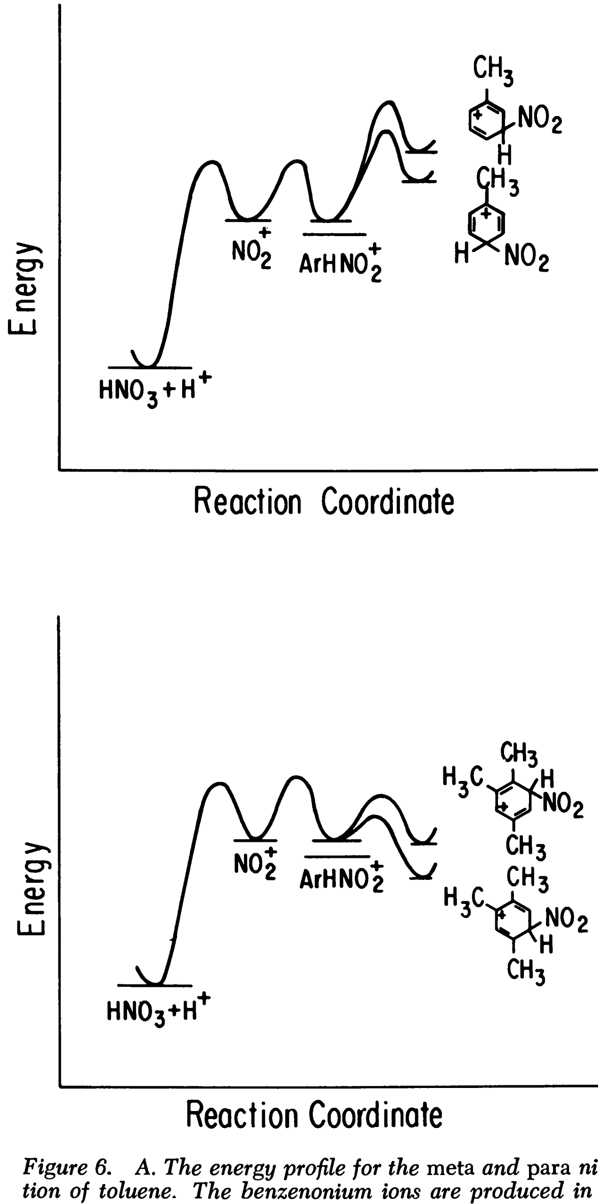


Figure 6. A. The energy profile for the meta *and* para *nitration of toluene. The benzenonium ions are produced in the rate determining step. The energy difference at the transition state is about 1700 cal. B. The energy profile for the 5 and 6 nitration of pseudocumene. The encounter complex is produced in the rate determining step. The energy difference at the transition state for the formation of the benzenonium ions is about 1200 cal.*

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Table VIII. Partial Rate Factors for the Substitution of Toluene[a]

Reaction	k_T/k_B	Partial Rate Factors			Ref.
		$\underline{o}_f$	$\underline{m}_f$	$\underline{p}_f$	
Acetylation					
CH_3COF,BF_3	130	4.7	4.3	762	35
$CH_3COCl,AlCl_3,CS_2$	141	10.5	8.4	808	35
$CH_3COCl,AlCl_3,C_2H_4Cl_2$	128	4.5	4.8	750	29b
Nitration					
$HNO_3,HOAc,H_2O$	24.5	42	2.5	58	29
HNO_3,CH_3NO_2	21.0	38.9	1.3	45.8	29
$AcONO_2,Ac_2O$	23.0	40	3.0	51	29
$HNO_3,HOAc$	28.8	49	2.4	70	29a
$HNO_3,C_4H_8SO_2$	17.0	32	1.7	35	29a
$HNO_3,H_2SO_4,C_4H_8SO_2$	28.0	52.1	2.8	58.1	29a
HNO_3,CF_3CO_2H	28.0	51.7	2.2	60.1	29a
Chlorination					
$Cl_2,HOAc$	340	617	5.0	820	29b
Cl_2,CF_3CO_2H	464	928	6.5	928	29b
$HOCl,HClO_4$	60	134	4.0	82	29b
$Cl_2,ICl,C_2H_4Cl_2$	230	430	(7.8)[b]	520	36
$Cl_2,SnCl_4,C_2H_4Cl_2$	165	360	(5.4)[b]	270	36
$Cl_2,FeCl_3,CH_3NO_2$	55	110	3.8	100	36
$AcOCl,HClO_4,HOAc,H_2O$	145	306	(3)[b]	237	37

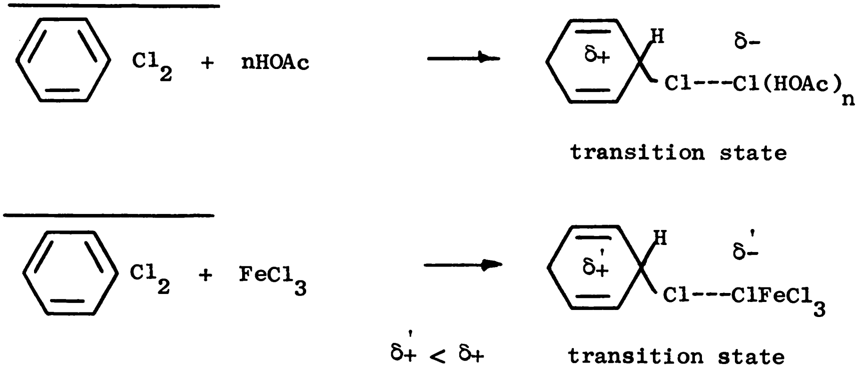
[a] The reactions were, for the most part, carried out at 25°.

[b] Estimated by additivity approach.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

actions the relative rates and product distributions for the substitution of toluene, for example, are nearly constant even though the absolute reaction rates vary enormously.[38] This feature is well illustrated by the fact that the antimony pentachloride-catalyzed benzoylation reaction proceeds about 1300-fold more rapidly than the aluminum chloride-catalyzed reaction, yet the product distributions for toluene are the same.[38b] Also the $\underline{p}_f^{CH_3}$ values for boron trifluoride-catalyzed acetylation of toluene with acetyl fluoride and for the aluminum chloride-catalyzed acetylation of toluene with acetyl chloride are very similar.[35]

In sharp contrast, the relative rates, isomer distributions, and partial rate factors for chlorination depend importantly on the character of the reagent and catalysts. The order-of-magnitude differences in $\underline{p}_f^{CH_3}$ indicate that there are important variations in the energy content of the transition states leading to the possible benzenonium ions. The invariance in the



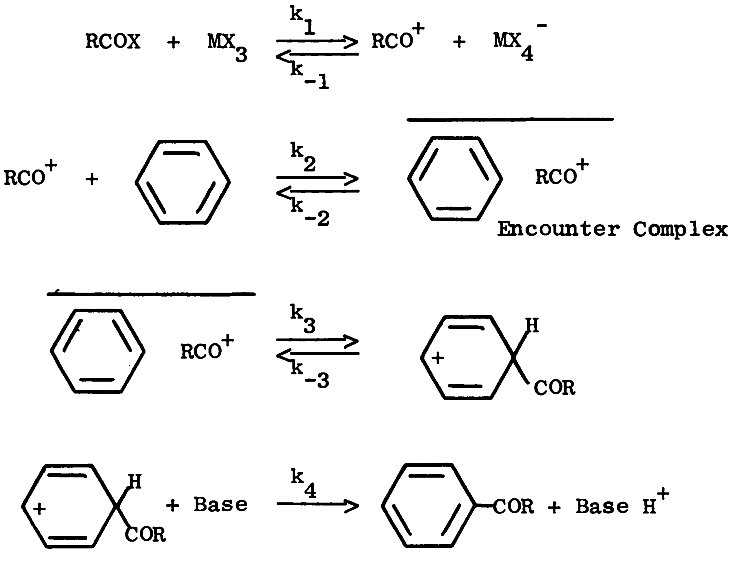
partial rate factors for acylation, on the other hand, can be comfortably identified with a reaction mechanism in which the acylonium ion is produced in a prior step and subsequently reacts in a rate determining process with the aromatic compound, Mechanism IV.

The mechanisms for nitration and acetylation, II and IV, are very similar. Both reactions proceed via an electrophilic intermediate with the differences in product distributions resulting from the variations in the energy requirements for the formation of the various benzenonium ions.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Mechanism IV



The large negative ρ^+ value, -9 for acetylation compared to -6 for nitration,[29b] reflects the greater energy requirements for the conversion of the encounter pair, $\overline{\text{ArH RCO}^+}$, to the benzenonium ions. There is no evidence for the rate determining formation of the encounter complex even for the polymethylbenzenes.[39]

In summary, the available data suggest that the product distributions in the nitration reactions are defined by the kinetically controlled rates of formation of the possible benzenonium ion reactions even though different rate limiting reactions are involved in the overall process. The comparison of nitration, acetylation, and chlorination suggests that nitration and acetylation follow quite similar reaction paths. This Friedel-Crafts reaction is more selective than nitration but the differences in reactivity are manifest in the same key step - the formation of the benzenonium ions.

The Encounter Complex

The early work on the nitronium salt nitration reactions prompted Olah and his associates to propose that pi complexes were produced in the rate determining step of the reaction.[6,40] More recently, Olah and Lin have argued that the relative rates of nitration in the boron trifluoride-catalyzed reaction of methyl nitrate with aromatic compounds and in the nitronium salt nitration reactions are parallel to the relative stabilities of

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

pi complexes between the hydrocarbons and hydrogen chloride.[28] Rys, Skrabal and Zollinger have examined this viewpoint in considerable detail.[17]

The results presented in Table IX illustrate the pattern of reactivity.

Rys, Skrabal, and Zollinger conclude, as discussed in a prior section, that mixing rates render the relative rate data for nitronium salt nitration valueless for the definition of chemical reactivity patterns. It is also clear that the boron trifluoride-catalyzed reactions of methyl nitrate with the polymethylbenzenes reach a limiting value, about 1000, signaling the onset of encounter control as noted previously. Accordingly, neither set of data can reliably be used to infer the involvement of pi complex intermediates. They also tested various linear free energy relationships and concluded in each case that there was no reliable correlation between the results for nitration and pi complex stability.[17]

Moodie, Schofield and Weston have also commented on this point. They note that the selectivity observed in the reactions of the activated aromatic compounds can be quite readily rationalized without requiring an attractive interaction in the encounter complex.[31] Inasmuch as the energy barrier for separation of the encounter complex may exceed 3 kcal mole.$^{-1}$ in the sulfuric acid solvents, there is an ample energy range for selectivity in the formation of the benzenonium ion.

In brief, the available data are mute concerning the existence or non-existence of attractive interactions in the encounter complex. There is no substantive support for the view that these entities should be characterized as pi complexes.

Conclusion

The contributions of several groups have provided important information concerning the mechanism of the nitration reaction. It is now recognized that mixing effects render the nitronium salt nitration data inexact and that diffusion processes prevent the acquisition of meaningful relative rate data for the reactive compounds. These two complications offuscate many chemically significant events. Careful kinetic studies and accurate determinations of the product distribution provide the basis for renewed faith in the general nature of the nitronium ion nitration mechanism, II, with the interesting feature of encounter control for sufficiently reactive molecules.

Acknowledgement

It is a pleasure to acknowledge the able typing effort of Mrs. Mary Brown and the support of the Block Fund of the University of Chicago in the preparation and presentation of this review.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Table IX. Relative Rates, Nitration Product Ratios, and Pi Complex Stability

Compound	Relative Rate Bromination[a] Br_2, 85% HOAc	Relative Stability Protonation[b] HF, BF_3	Product Ratio Nitration[c] NO_2BF_4, $C_4H_8SO_2$	Product Ratio Nitration[d] CH_3ONO_2, CH_3NO_2	Relative Stability Pi Complex[e] HCl, n-C_7H_{16}
Benzene	1.00	1.00	1.00	1.00	1.00
Toluene	605	790	1.67	25.5	1.51
o-Xylene	5.3×10^3	7.9×10^3	1.75	192	1.81
m-Xylene	5.1×10^5	1.0×10^6	1.65	285	2.06
p-Xylene	2.5×10^3	3.2×10^3	1.96	295	1.65
1,2,3-Trimethylbenzene	1.6×10^6	2.0×10^6		914	2.40
1,2,4-Trimethylbenzene	1.5×10^6	2.0×10^6		1.1×10^3	2.23
1,3,5-Trimethylbenzene	1.9×10^8	6.3×10^8	2.71	956	2.60
1,2,3,4-Tetramethylbenzene	1.1×10^7	2.0×10^7		2.1×10^3	2.68
1,2,3,5-Tetramethylbenzene	4.2×10^8	2.0×10^9		1.9×10^3	2.74
1,2,4,5-Tetramethylbenzene	2.8×10^6	1.0×10^7		2.2×10^3	2.86
Pentamethylbenzene	8.1×10^8	2.0×10^9			

[a] Ref. 41. [b] Ref. 42. [c] Ref. 6. [d] Ref. 28. [e] Ref. 43.

Literature Cited

(1) C.K. Ingold, "Structure and Mechanism in Organic Chemistry," Chapter 6, Cornell University Press, 1953.

(2) J.G. Hoggett, R.B. Moodie, J.R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge University Press, 1971.

(3) Bird, M.L. and Ingold, C.K., J. Chem. Soc. (1938) 1959.

(4) Stock, L.M. and Brown, H.C., Adv. Phys. Org. Chem., (1963), 1 35.

(5) The results for these reactions are summarized in ref. 4. The data for the nitration reaction were developed, in large part, by C.K. Ingold and his students. The data for acid-catalyzed hypobromous acid bromination were obtained by P.B.D. de la Mare and his associates.

(6) Olah, G.A., Kuhn, S.J. and Flood, S.H., J. Amer. Chem. Soc., (1961), 83, 4511.

(7) The low relative rate value is obtained reproducibly even when the concentrations of the reagents are altered. This feature of the results is discussed in ref. 2, p. 66, and by Ridd and his associates, ref. 14.

(8) For a more complete summary, Olah, G.A., Accounts of Chem. Res., (1971), 4, 240.

(9) Ingold, C.K. and Shaw, F.R., J. Chem. Soc., (1927), 2918.

(10) T.S. Lee, "Investigation of Rates and Mechanisms of Reactions," S.L. Friess and A. Weissberger, editors, "Technique of Organic Chemistry," Volume VIII, 1st Edition, Interscience Publishers, Inc., New York (1953), p. 100.

(11) Wei, J., J. Catalysis, (1964), 3, 299.

(12) Tolgyesi, W.S., Can. J Chem., (1965), 43, 343.

(13) Olah, G.A. and Overchuck, N.A., Can. J. Chem., (1965), 43, 3279.

(14) Christy, P.F., Ridd, J.H. and Stears, N.D., J. Chem. Soc. B, (1970), 797.

(15) Gastaminza, A. and Ridd, J.H., J. Chem. Soc., Perkin II, (1972), 813.

(16) Ridd, J.H., Accounts Chem. Res., (1971), 4, 248.

(17) Rys, P., Skrabal, P. and Zollinger, H., Angew. Chemie Internat. Ed., (1972), 11, 874.

(18) Coombes, R.G., Moodie, R.B. and Schofield, K., J. Chem. Soc. B, (1968), 800.

(19) Hoggett, J.B., Moodie, R.B. and Schofield, K., J. Chem. Soc. B, (1969), 1

(20) Coombes, R.G., Moodie, R.B. and Schofield, K., J. Chem. Soc. B, (1969), 52.

(21) Coombes, R.G., Crout, D.H.G., Hoggett, J.G., Moodie, R.B., and K. Schofield, J. Chem. Soc. B, (1970), 347.

(22) Chapman, J.W. and Strachan, A.N., J. Chem. Soc.·Chem. Comm., (1974), 293.

(23) (a) Ref. 2, p. 63. (b) Ref. 4, p. 50.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

(24) The role of encounter controlled reactions in chemical kinetics has been considered by (a) R.M. Noyes, "Progress in Reaction Kinetics," Pergamon Press (1961). (b) North, A.M., Quart. Revs., (1966), 20, 421.

(25) Coombes, J. Chem. Soc. B, (1969), 1256.

(26) Hartshorn, S.R., Moodie, R.B., Schofield, K. and Thompson, M.J., J. Chem. Soc. B, (1971), 2447.

(27) Marziano, N.C., Rees, J.H. and Ridd, J.H., J. Chem. Soc., Perkin II, (1974), 600.

(28) (a) Olah, G.A. and Lin, H.C., J. Amer. Chem. Soc., (1974), 96, 2892, report that 1% of the meta isomer is obtained. (b) Coombes, R.G. reported at the Symposium that none of this isomer could be detected under the experimental conditions. The detection limit was 0.003%.

(29) (a) Ref. 2, p. 64. (b) Ref. 4, p. 50.

(30) Coon, C.L., Blucher, W.G. and Hill, M.E., J. Org. Chem., (1973), 25, 4243.

(31) Moodie, R.B., Schofield, K. and Weston, J.B., J. Chem. Soc. Chem. Comm., (1974), 382.

(32) Myhre, P.C., J. Amer. Chem. Soc., (1972), 94, 7921.

(33) (a) Hahn, R.C. and Groen, M.B., J. Amer. Chem. Soc., (1973), 95, 6128. (b) Fischer, A. and Greig, C.C., J. Chem. Soc. Chem. Comm., (1974), 50. (c) Fischer, A. and Ramsay, J.N., Can. J. Chem., (1974), 52, 3960.

(34) It should be emphasized that this conclusion is based on the idea that the rearrangement reactions of the ions are slow relative to the rate of proton loss. This condition may not be satisfied under all circumstances.

(35) Olah, G.A. and Kobayashi, S., J. Amer. Chem. Soc., (1971), 93, 6964.

(36) Stock, L.M, unpublished results.

(37) dela Mare, P.B.D., Hilton, I.C. and Varma, S., J. Chem. Soc., (1966), 4044.

(38) (a) The acylation reaction is discussed by G.A. Olah, "Friedel-Crafts and Related Reactions," Volume I, p. 91-115 (1963). (b) Jensen, F.R. and Brown, H.C., J. Amer. Chem. Soc., (1958), 80, 3044.

(39) Marino, G. and Brown, H.C., J. Amer. Chem. Soc., (1959), 81, 5929.

(40) Several variations on this proposal have been advanced by Olah and his associates. See ref. 17 for a critical evaluation of the idea.

(41) Brown, H.C. and Stock, L.M., J. Amer. Chem. Soc., (1957), 79, 1421.

(42) Mackor, E.L., Hofstra, A. and vander Waals, J.H., Trans Fara. Soc., (1958), 54, 66, 187.

(43) Brown, H.C. and Brady, J.D., J. Amer. Chem. Soc., (1952), 74, 3570.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch002

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

3

Selectivity in Aromatic Nitration

ROBERT G. COOMBES,* JOHN G. GOLDING, LESLIE W. RUSSELL
and GEOFFREY D. TOBIN

Department of Chemistry, The City University, London EC1V 4PB, England

Some recent observations on the intramolecular and intermolecular selectivity of some nitrating agents are presented in summary form in this paper. Attention will be concentrated on nitration by nitric acid in aqueous sulphuric acid, and by way of introduction reference will be made both to our own earlier studies and also to those of other workers in this field. It will become apparent that a situation of increasing complexity is being gradually revealed.

It is well established (1,2,3,4,5) that there exists a limiting rate of nitration of aromatic compounds which occurs at about the same threshold of aromatic reactivity in several nitration media. This limit was first observed (1) for nitration by nitric acid in aqueous sulphuric acid and in this medium the observed limit is in good agreement with a value calculated from diffusion theory for the rate of diffusion together or encounter of nitronium ions and substrate molecules. Only in aqueous sulphuric acid is it possible to make the estimate of nitronium ion concentration which makes the calculation possible. It was therefore suggested that the rate-determining step for nitration changes at the limit to the one in which the encounter pair is formed (Figure 1).

By analogy with literature discussions (6) of diffusion-controlled processes it was implied that there was no interaction within the encounter pair. If this were the case, as k_{-1} can be estimated (7) as about 10^9-10^{10} s^{-1} and k_2 can in the limit approach 10^{12} - 10^{13} s^{-1}, it would be possible for considerable intramolecular selectivity to remain between positions in a substrate which are sufficiently reactive to be nitrated at the limiting rate.(8)

Another suggestion (9,10) has been that the existence of the limiting rate might be explained by what has been called the Hammond Effect. As one increases the reactivity along a series of suitable substrates the transition state will become

---

*Author to whom correspondence should be addressed.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

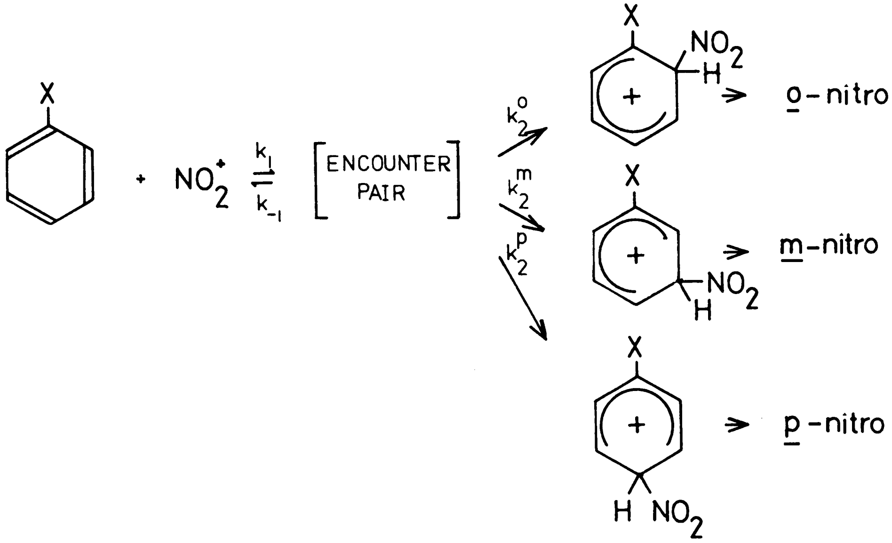
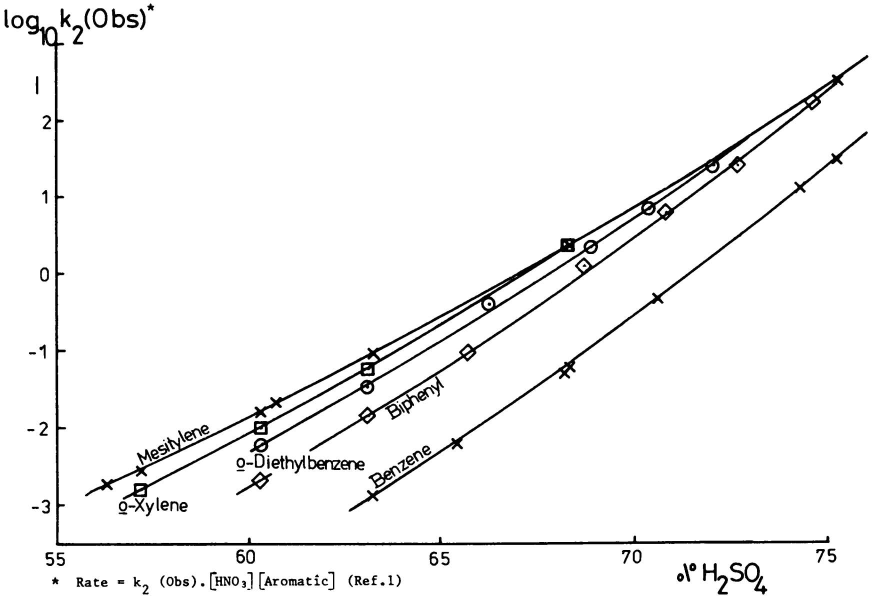


Figure 1.



* Rate = k_2 (Obs).[HNO_3][Aromatic] (Ref.1)

Figure 2.

progressively earlier, bonding from the electrophile to the carbon atom increasingly less developed and the activation energy lower until differences might have effectively disappeared. It has been envisaged that these transition states might be positionally oriented (10) and in this circumstance selectivity between sufficiently reactive positions should disappear at the limiting rate. This would also be the situation if there existed separate encounter pairs for different positions of substitution in a molecule. (11)

If these early transition states are not positionally oriented the existence of a common discrete intermediate, prior to formation of Wheland intermediates, seems obligatory and therefore the suggestion would be of a change in rate-determining step to that of formation of this intermediate.

Recent expressions (10, 12) of these ideas suggest that the intermediate has in fact an oriented π-complex type of structure. Energy diagrams have been drawn (12) showing the possible Wheland intermediates for a substitution resulting from one common π-complex structure presumably of this type. For it to be necessary to postulate a change of rate-determining stage to one in which an intermediate which involves attractive interaction is formed, an intramolecular selectivity greater than that possible for a non-interacting encounter pair would have to be observed. (8)

On other occasions (10) the oriented π-complex type of structure has been drawn as a representation of early transition states of the positionally oriented type to which the previous arguments would apply.

The present evidence on these points comes from published work (8)of Moodie, Schofield and their group at the University of Exeter. They have studied the nitration of pseudocumene and have shown that there is about a 9:1 selectivity of attack on positions 5 and 6 provided that one makes the reasonable assumption that any *ipso*-attack is not followed by rearrangement under the chosen conditions. Both positions are reactive enough to achieve the limiting rate and have similar steric requirements. This deduction rules out the explanation in terms of early transition states of the positionally oriented type and also precludes the possibility of detectable positionally oriented intermediates prior to the Wheland intermediates. It means that there must be a common intermediate prior to Wheland intermediate formation, but the extent of intramolecular selectivity is certainly not sufficient to make it necessary to postulate any attractive interaction in this intermediate.

Our initial approaches (11, 13) to these problems involved substrates where it seemed that a change in the rate-determining stage of reaction might have occurred over a range of concentrations of aqueous sulphuric acid due to the change in solvent viscosity. For example, we studied *o*-xylene (11) and *o*-diethylbenzene (13) for which rate profiles are shown in

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

Figure 2* compared with that of mesitylene (1,11). Mesitylene reacts at the limiting rate and the profiles for *o*-xylene and *o*-diethylbenzene become indistinguishable from that of mesitylene above about 68 and 73% H_2SO_4 respectively.

Contrary to general assumption it was clear that the ratio of isomers from these aromatics, which have simple alkyl substituents, changed considerably with acidity in aqueous sulphuric acid. The major factor in these changes was elegantly demonstrated by Professor P.C. Myhre (14) who showed that for *o*-xylene considerable initial *ipso* - attack occurs at a carbon atom bearing a methyl group leading to a Wheland intermediate which rearranges at high acidities eventually to form 3-nitro-*o*-xylene and is captured by a nucleophilic species at lower acidities to produce products that had escaped us in our studies (Figure 3). It has therefore become necessary to study not product nitrocompound ratios but yields of the various nitroproducts.

The nitration of *o*-xylene has been reinvestigated in this way by Moodie, Schofield *et al.* (15) By extrapolation of their results and combination with those of Professor Myhre, it is possible to calculate the proportion of attack at the *ipso* and 3-positions and to see that these vary considerably with acidity as does the attack at position 4 which can be directly measured (Table I). These changes have been attributed to a strong medium dependence of the relative reactivities of the various substituted and unsubstituted positions in the molecule. (15)

TABLE I

% ATTACK AT POSITIONS IN *o*-XYLENE

				Toluene
% H_2SO_4	% C-*ipso*	% C-3	% C-4	% C-4
50	73	8	19	30
60	60	12	28	32
70	45	18	37	34
80	-	-	45	38

The magnitude of these effects however is surprisingly high. For example one can compare these results with corresponding data for toluene (15) (Table I). Here a smaller dependence of isomer yield on acidity is apparent, and the % *meta*-substitution in toluene remains almost constant.

---

* All rate and product data quoted in this paper are from reactions at 25°C and at very low aromatic concentration, typically 10^{-4} mole l^{-1}, unless otherwise stated.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

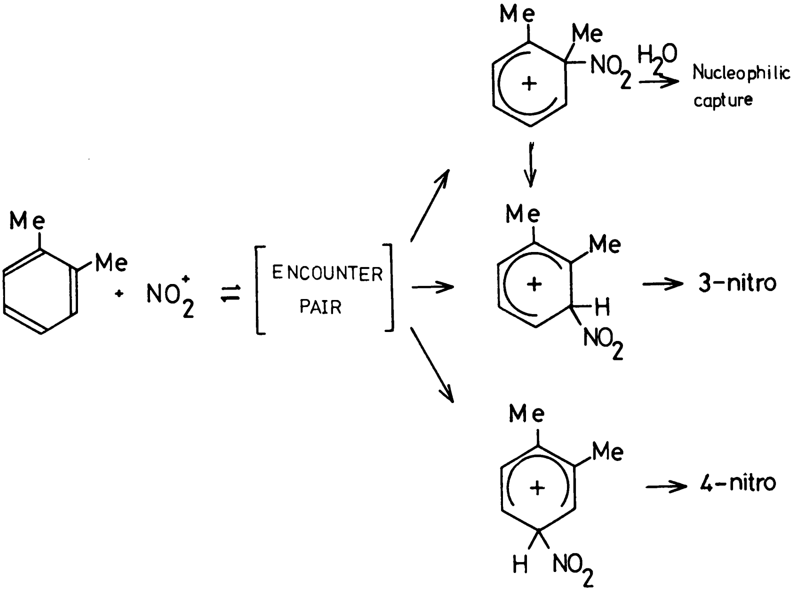


Figure 3.

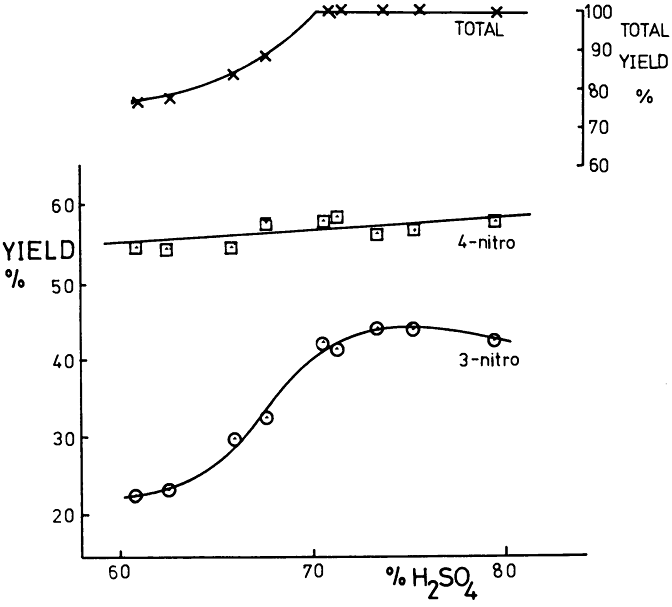


Figure 4. Nitration of o-*diethylbenzene*

Solvation effects have been invoked in the past to explain anomalous results from electrophilic substitution reactions of o-xylene and some similar compounds, (16) the effects depending on the presence of two groups ortho to one another. The application of any related ideas receives little support from our study of o-diethylbenzene. (13) The results of this are shown in Figure 4.

This shows a plot of the yield of each nitroproduct against % H_2SO_4 and also incorporated is an indication of total yield of nitroproducts recovered. All data are based on the initial quantity of aromatic compound. Quantitative yields of the nitroproducts are obtained above about 70% H_2SO_4 and the drop in yield and in the amount of 3-substitution below that acidity can be attributed to nucleophilic capture of the ipso - substituted Wheland intermediate. The change in amount of 4-substitution is however much less than the corresponding change for o-xylene. For o-diethylbenzene the combination of 3- and ipso-substitution is less at all acidities presumably for steric reasons. o-Xylene then behaves in a way, even when ipso - substitution is allowed for, that would be unsuspected from a study of toluene or o-diethylbenzene.

These initial studies of intramolecular selectivity of alkyl compounds which react at or near the limiting rate and the interesting developments that ensued prompted us to extend our studies to methoxy substituted aromatics. (17)

Anisole is nitrated at a rate which is shown in Figure 5. The profile is parallel to that of mesitylene and the rate is about half that for mesitylene under similar conditions. The product data are shown in Figure 6. The occurrence of nitration via nitrosation which has been shown to have complicated many previous studies of anisole was precluded. The results are remarkable; the % 4-substitution increases over the range up to 82% H_2SO_4 and the % 2-substitution decreases correspondingly, $< 10^{-3}$ % of 3 - nitroanisole is formed in these reactions. Presumably a strong medium effect on the substituent effect of the methoxy group is being observed. This is consistent with changes observed (18) in the ultraviolet absorption spectra of anisole in this region of acidity which are most reasonably interpreted in terms of an interaction with the medium.

The situation in above 82% H_2SO_4 is not clear. The total yield drops and this appears to be due to the formation of less 4-nitroanisole than could be expected by extrapolation. 2- and 4-nitroanisole can be extracted quantitatively from simulated reaction solutions.

Arguments which associate isomer ratio changes for anisole with a change of electrophile must be scrutinized most carefully.

One might imagine that these comprehensive data on anisole would enable us to predict the intramolecular selectivity of nitration of veratrole (1,2-dimethoxybenzene) with some success. Veratrole is nitrated at the limiting rate (Figure 5). (19) The

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

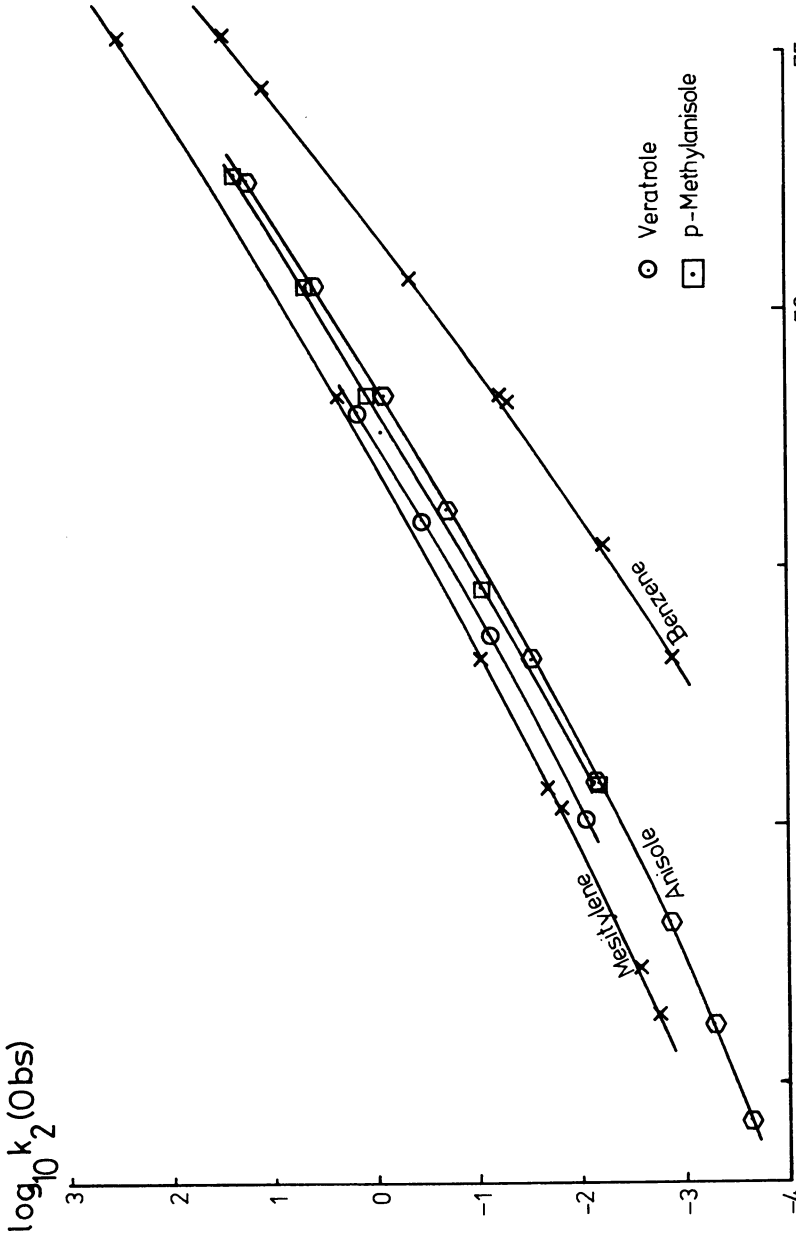


Figure 5.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

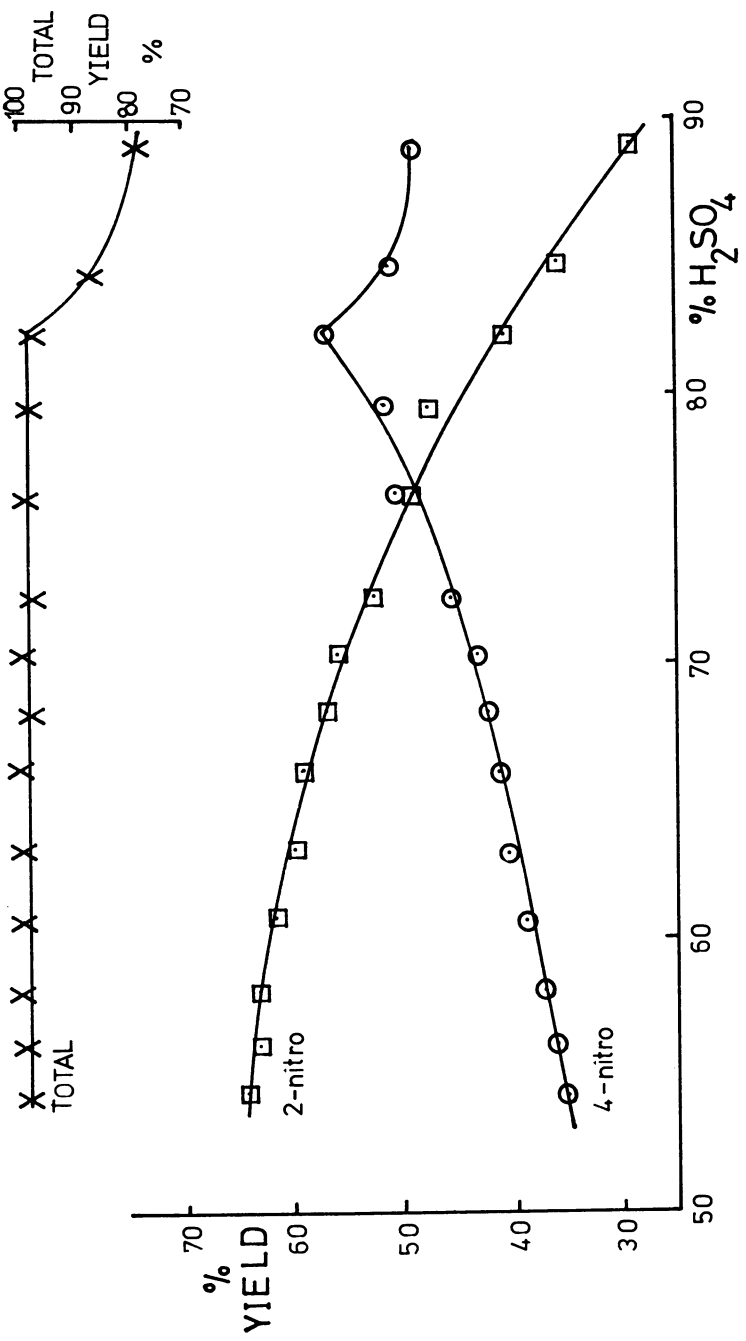


Figure 6. Nitration of anisole

profile lies between those of anisole and mesitylene and is approximately parallel to them. 3-Nitroveratrole was not detected in the products and was certainly less than 0.5% of the yield. Nitration produced only 4-nitroveratrole in 92-98% yields over the range 60-75% H_2SO_4. Nitration via nitrosation was precluded from these reactions. Clearly the juxtaposition of the methoxy groups has produced an effect far removed from that expected from consideration of their behaviour in isolation.

A study of the nitration of p-methylanisole (17) has also provided anomalous results. The rate profile for this compound which is also nitrated at the limiting rate is shown in Figure 5. It is almost identical with that of anisole. The reasons for the small spread of apparent reactivity of the group of compounds at the limiting rate in Figure 5 is not known. The product data are shown in Figure 7. Two products are formed in constant proportion and quantitative yield over a wide range of acidity. These products are also formed in this constant proportion during individual runs. The major product is 2-nitro-4-methylanisole and this is the product one would expect in the absence of ipso - substitution. The second product is 2-nitro-4-methylphenol and this is not formed either by demethylation of p-methylanisole before nitration or of 2-nitro-4-methylanisole after nitration.* The Wheland intermediate involving ipso-attack at the methyl group must be formed and Figure 8 is suggested as a possible route for reaction. Rate-determining encounter pair formation is followed by normal nitration or by formation of the ipso-substituted Wheland intermediate. Overall demethylation to a cyclohexadienone intermediate followed by protonation and loss of nitronium ion gives p-cresol. This will be nitrated at the limiting rate and so the nitronium ion will not leave the solvent cage.

If, however, 2-nitro-4-methylphenol is the result of ipso-attack para to the methoxy group there is no evidence for the change of the methoxy group substituent effect with acidity which was apparent with anisole itself.

The picture that emerges from these studies so far then is that the dominant factors affecting the change in yields from particular reactive positions in a substrate are those associated with ipso-substitution and with medium effects. The latter are often for an as yet unknown reason considerably more important than one might expect.

In the remaining section nitration (21) by dinitrogen tetroxide in dry carbon tetrachloride solution is considered. Typical data are shown in Table II. There appear to be two distinct types of reaction with toluene. The first is apparent at low concentrations of N_2O_4 (< about 0.2 mole l^{-1}) where product isomer distributions characterized by a high percentage of m-nitrotoluene were observed. At high N_2O_4 concentrations

* A similar phenomenon occurs with p-methylanisole (23) and also p-chloroanisole (20) on nitration in acetic anhydride.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

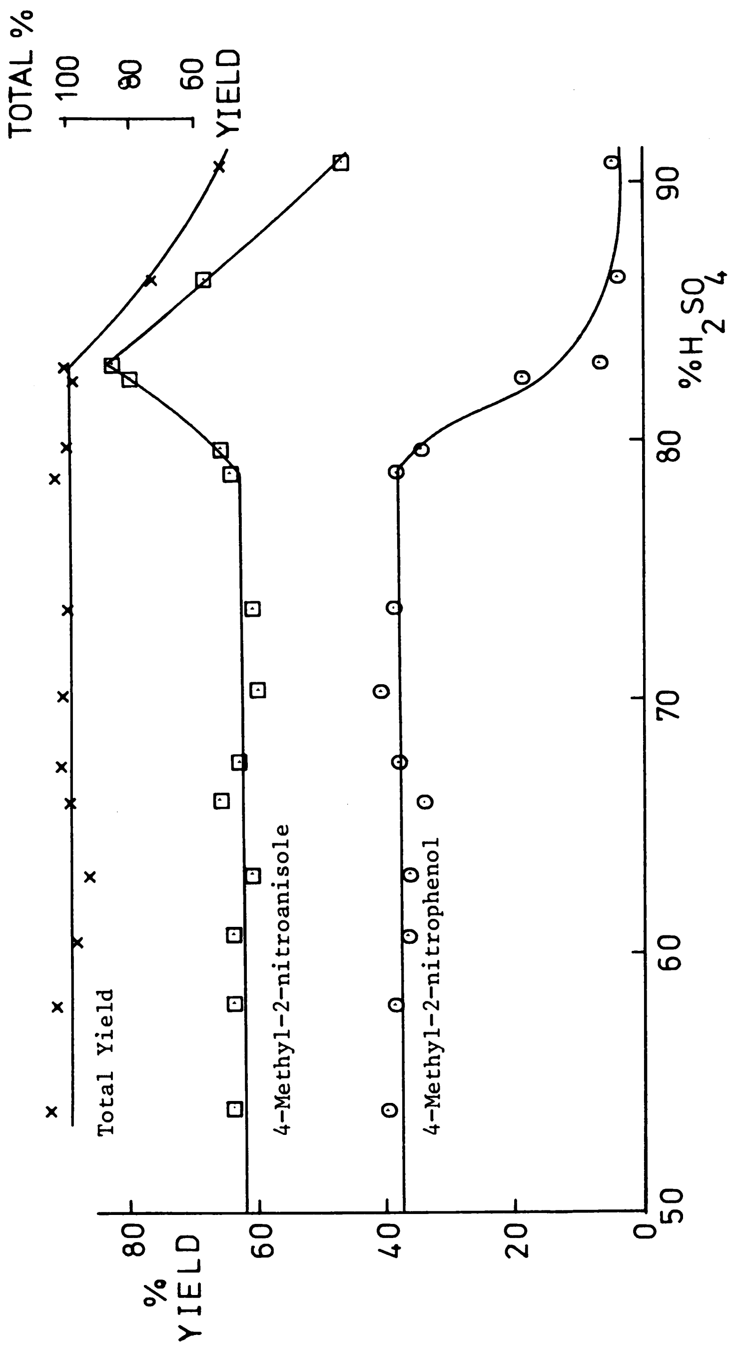
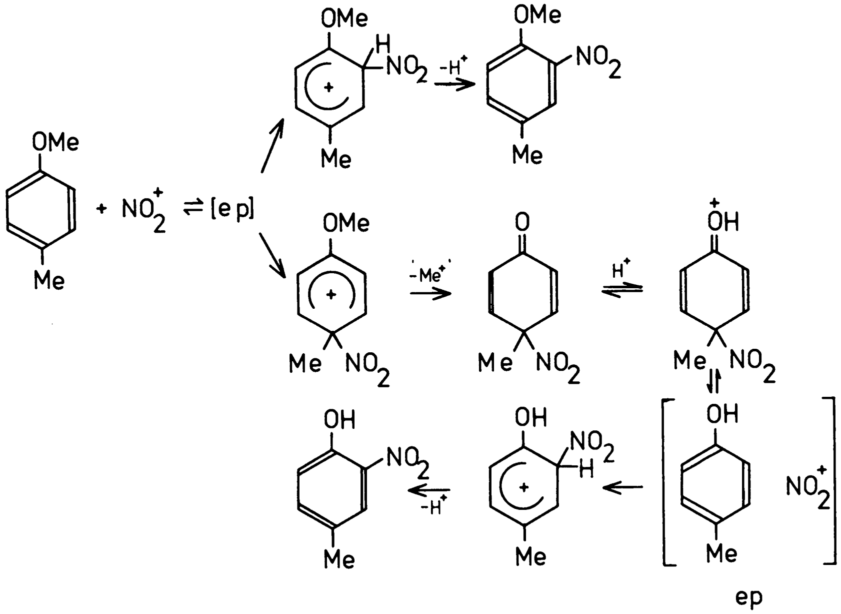


Figure 7. Nitration of p-*methylanisole*

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003



ep ≡ Encounter pair

Figure 8.

TABLE II

INTRAMOLECULAR SELECTIVITY OF N_2O_4 IN CCl_4 AT 20°

$[N_2O_4]$	[ArH]	% yield	nitrocompound % o	m	p
Toluene					
0.02	0.4	6	39	44	17
1.2	3.5	4	48	3	49
Ethylbenzene					
0.2	0.6	(a)	5	90	5
t-Butylbenzene					
0.2	0.6	(a)	35	15	50

(a) 0.5 - 5%

(∿ 1 mole l^{-1}) however the operation of an electrophilic mechanism with low proportions of m-nitrotoluene was indicated. At intermediate concentrations reactions initially yielded a high proportion of m-nitrotoluene but as the reaction proceeded the values began to resemble an isomer distribution expected for electrophilic attack. Reactions were slow at room temperature at all concentrations and low conversions (∿ 5%) were achieved. Other products including benzaldehyde, benzyl alcohol and phenylnitromethane were formed, although the ring nitrocompounds were not intermediates in the formation of these or other products. Unusual isomer proportions at low N_2O_4 concentrations also occurred with other alkyl benzenes (Table II). Ethylbenzene gave a high proportion of meta-nitration and t-butylbenzene high ortho-nitration.

A most reasonable interpretation of these results would be that the reactive entity is some species, perhaps radical in nature, which shows a very different intramolecular selectivity from that of the nitronium ion. The efficacy of nitrogen dioxide itself appears ruled out, however, by the low conversions. Study of the intermolecular selectivity of the reagent by competition (Table III) indicates that the reagent is about as selective as the nitronium ion between alkylbenzenes. The relative rates observed are compared with two systems (1,2,11,22) where the nitronium ion is well established as the electrophilic species. For toluene the unusual isomer ratios were observed in these competition runs.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

TABLE III

INTERMOLECULAR SELECTIVITY

	HNO_3 in 57% H_2SO_4[a]	HNO_3 in aq $MeNO_2$[a]	N_2O_4 in CCl_4[b]
Mesitylene	135	400	280
o-Xylene	90	139	100
Toluene	17	25	40
Benzene	1	1	1
Chlorobenzene	0.06	0.03	0.2

a 25°
b 20°

We are therefore faced with an anomalous situation. A gross change of the reactive species from the nitronium ion is indicated by the results of study of intramolecular selectivity but this change would have gone unsuspected if reliance had been placed solely on the evidence of intermolecular selectivity.

In conclusion we would express our gratitude to the S.R.C. for financial support (J.G.G. and L.W.R.) and to the Physico-Chemical Measurements Unit at Harwell.

Dr. R.B. Moodie and Professor K. Schofield are thanked for their guidance in the past and for communication of results prior to publication.

Literature Cited

(1) Coombes, R.G., Moodie, R.B. and Schofield, K. J.Chem. Soc.(B), (1968), 800.
(2) Hoggett, J.G., Moodie, R.B. and Schofield, K. J.Chem. Soc.(B), (1969), 1.
(3) Coombes, R.G. J.Chem.Soc.(B), (1969), 1256.
(4) Hartshorn, S.R., Moodie, R.B., Schofield, K. and Thompson, M.J. J.Chem.Soc.(B), (1971), 2447.
(5) Hartshorn, S.R., Hoggett, J.G., Moodie, R.B., Schofield, K. and Thompson, M.J. J.Chem.Soc.(B), (1971), 2461.
(6) North, A.M. 'The Collision Theory of Chemical Reactions in Liquids', Methuen, London, 1964.
(7) Amdur, I, and Hammes, G.G. 'Chemical Kinetics', p.63, McGraw-Hill, London, 1966.

(8) Moodie, R.B., Schofield, K. and Weston, J.B. J.C.S.Chem. Comm., (1974), 382.

(9) Hartshorn, S.R. and Schofield, K. 'Progress in Organic Chemistry', 8, p.278, Butterworth, London, 1973.

(10) Olah, G.A., Kobayashi, S. and Tashiro, M. J.Amer.Chem.Soc. (1972), 94, 7448.

(11) Coombes, R.G. and Russell, L.W. J.Chem.Soc.(B), (1971), 2443.

(12) Olah, G.A. Acc.Chem.Res., (1971), 4, 240.

(13) Coombes, R.G. and Tobin, G.D. unpublished results.

(14) Myhre, P.C. J.Amer.Chem.Soc., (1972), 94, 7921.

(15) Barnett, J.W., Moodie, R.B., Schofield, K. and Weston, J.B. J.C.S. Perkin II, (1975), 648.

(16) Ansell, H.V. and Taylor, R. J.Chem.Soc.(B), (1968), 526.

(17) Barnett, J.W., Coombes, R.G., Golding, J.G., Moodie, R.B., Schofield, K. and Tobin, G.D. to be published.

(18) Arnett, E.M. and Wu, C.Y. J.Amer.Chem.Soc., (1960), 82, 5660; Svanholm, U. and Parker, V.D. J.C.S. Perkin II, (1972), 961.

(19) Coombes, R.G. and Golding, J.G. unpublished results.

(20) Perrin, C.L. and Skinner, G.A. J.Amer.Chem.Soc., (1971), 93, 3389.

(21) Russell, L.W. Ph.D. Thesis, The City University, London, 1974.

(22) Coombes, R.G., Crout, D.H.G., Hoggett, J.G., Moodie, R.B. and Schofield, K. J.Chem.Soc.(B), (1970), 347.

(23) Shabarov, Yu. S. and Mochalov, S.S. J. Org. Chem. (U.S.S.R.), (1973), 9, 2061.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch003

4

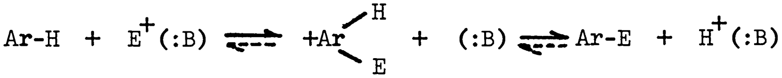
Some Representative Chemistry of *Ipso* Ions Formed During Aromatic Nitration

PHILIP C. MYHRE

Professor of Chemistry, Harvey Mudd College, Science and Engineering,
Claremont, Calif.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

The path of aromatic electrophilic substitution is frequently represented in the manner shown, eq 1. The reversible



$$\mathrm{Ar{-}H} + \mathrm{E}^{+}(:\mathrm{B}) \rightleftharpoons {}^{+}\mathrm{Ar}\begin{smallmatrix}\mathrm{H}\\ \mathrm{E}\end{smallmatrix} + (:\mathrm{B}) \rightleftharpoons \mathrm{Ar{-}E} + \mathrm{H}^{+}(:\mathrm{B}) \qquad (1)$$

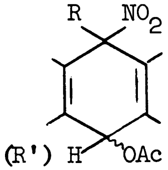
character of some aromatic substitutions is one demonstration that electrophilic attack is not restricted to aromatic carbon bearing hydrogen. Indeed, electrophilic attack at a substituent position (*ipso* attack) has been recognized for some time. It is now clear that the importance of such processes have not been appreciated fully.

The issue of *ipso* reactivity was placed in focus by Perrin and Skinner in 1971. (1) Shortly thereafter *ipso* reactivity was shown to be a major factor in nitration of a number of alkylbenzenes. (2,3,4) These data indicate that the cyclohexadienyl cations formed by attachment of the electrophile to aromatic carbon bearing an alkyl substituent are key intermediates, intermediates that provide rational explanations for many otherwise anomolous observations. The recent review by Hartshorn discusses a number of non-conventional aromatic substitutions. (5) A recurring theme in that review is electrophilic attack at a carbon bearing a substituent. It seems clear that detailed study of the chemistry of *ipso*-cyclohexadienyl cations is important if we are to gain a deeper understanding of aromatic electrophilic substitution.

Such studies are made more easily if the desired *ipso* ions can be generated in the absence of the isomeric cyclohexadienyl cations that typically form in direct aromatic substitution. This is now possible thanks to the results of Fischer and co-workers who found that nitration of many alkylbenzenes in solvent

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

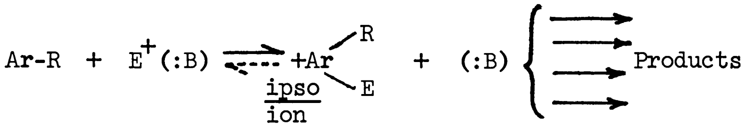
systems containing acetic anhydride yields 1,4-adducts of the type shown. (6) These cyclohexadiene derivatives presumably form in a two-step process involving electrophilic attack at an ipso carbon followed by nucleophilic quenching. It follows that the yield of adduct is a measure of the importance of ipso attack. Furthermore, the chemical consequences of ipso attack in various solvent systems can be determined by solvolytic regeneration of a cyclohexadienyl cation from the isolated 1,4-adduct.



where R and R' = alkyl or other electron donor groups

Chemical Consequences

Consideration of a cyclohexadienyl cation of the type shown in eq 2 where R and E are not readily lost as positively charged species should make clear the point that the reaction manifold so characteristic of carbonium ions is to be expected.

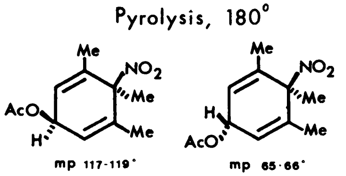


$$\mathrm{Ar{-}R} + \overset{+}{\mathrm{E}}(:\mathrm{B}) \rightleftharpoons \underset{\text{ipso ion}}{{}^{+}\mathrm{Ar}\begin{smallmatrix}\mathrm{R}\\ \mathrm{E}\end{smallmatrix}} + (:\mathrm{B}) \left\{\begin{matrix}\longrightarrow\\ \longrightarrow\\ \longrightarrow\\ \longrightarrow\end{matrix}\right. \text{Products} \qquad (2)$$

The reaction chemistry observed to date amply confirms this expectation. Because of the rich chemistry that can stem from ipso ions, it seemed important to us to select a tractable system and proceed to build a data base by examination of that system. With reference points established one can more profitably study structural variations and changes in reaction chemistry that attend such variation. The acetyl nitrate adducts derived from hemimellitene (1,2,3-trimethylbenzene) are particularly useful for this purpose. Both the cis and trans isomers may be rather easily isolated from nitration mixtures by low temperature crystallization procedures. The crystalline dienes thus obtained are stable in the cold and may be stored for long periods. The intent of the discussion that follows is to exemplify some of the chemistry of ipso ions by reference to some of our studies of the adducts of hemimellitene.

Pyrolysis. The thermal stability of the 1,4-nitro, acetoxy adducts of hemimellitene is limited. Decomposition occurs upon attempted gas-liquid chromatography, presumably in the injector oven region. In contrast with some other reports, we find that the major product of pyrolysis of the hemimellitene adducts is the parent hydrocarbon as shown in Figure 1.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004



%

ArH	82.0	56.5
5-AcOAr	16.3	42.5
4-NO_2Ar	1.7	1.0

Figure 1. Pyrolysis product distribution

The differences in product distribution shown by the cis and trans isomers suggest preferred, possibly concerted cis-elimination, but more detailed studies are required before firm conclusions may be drawn.

Solvolysis in Strong Acid. Solvolytic displacements involving these diene substrates can occur either by loss of acetate or by loss of the nitro group as nitrite, Figure 2. (2) Loss of acetate is required to regenerate the ipso ion formed during aromatic nitration. Strongly acidic media should favor this pathway since protonation of the more basic ester function provides a low energy path for departure of acetate as acetic acid.

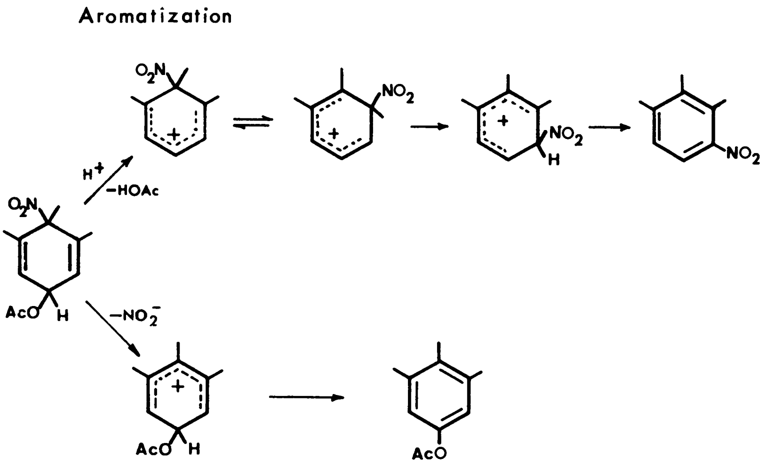


Figure 2. Some solvolitic pathways of aromatization

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

What chemistry is available to an *ipso* ion formed under these conditions? Nucleophilic quenching is precluded as is loss of either the methyl or the nitro group as a cation. Rearomatization can occur however by migration of the nitro group to a carbon bearing hydrogen and subsequent loss of a proton. The experimental demonstration of this reaction path was first preformed with the use of acetyl nitrate adducts of *o*-xylene (2), and a number of verifications have followed. The adducts of hemimellitene show similar solvolytic behavior. As shown in Figure 3, the yield of 4-nitrohemimellitene derived from

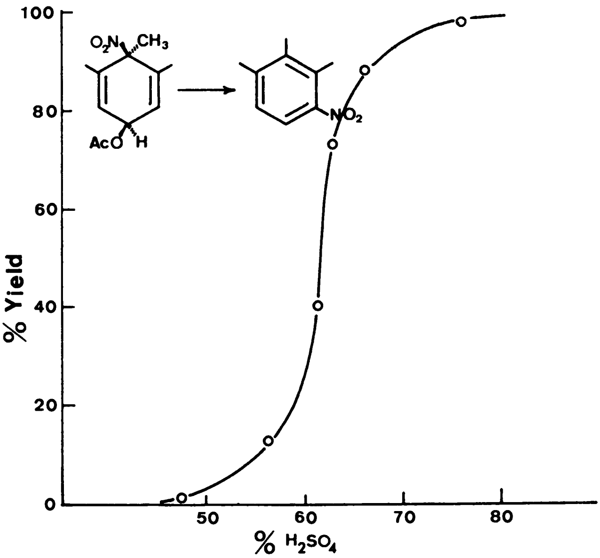


Figure 3. Yield of 4-nitrohemimellitene as a function of acid strength

solvolysis of *cis*-4-nitro-3,4,5-trimethylcyclohexa-2,5-dienyl acetate is nearly quantitative in sulfuric acid solutions in the 85 to 75% range, but the yield falls off rapidly through the 65 to 55% region and becomes sensibly zero below 50% sulfuric acid. It is important to note that no 5-nitrohemimellitene is detected as a product of solvolysis under any set of reaction conditions. Thus the path of nitro group migration seems best formulated as a sequence of 1,2-shifts, Figure 2.

These data and related studies previously reported (2,3) have important implications. First, they provide a rational explanation for certain changes in isomer distribution observed upon nitration in media of differing acid strength. Second, the data serve to place limits on the significance of partial rate factor data, since at least two independent paths can lead to the same nitroarene. (2) Previously it has been assumed that the percentage yield of a given nitration product was a direct

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

measure of the reactivity of a specific carbon site to the electrophilic reagent. We now know that this may not be the case. A high yield of a given nitroarene isomer may be fortuitous, a result of proximity of the site to substituent groups.

Solvolysis in Aqueous Systems. In weakly acidic hydroxylic solvents, nitrite ion is a better leaving group than acetate ion, and 1,4-adducts typically follow an aromatization path that leads to the formation of an aryl acetate and the elements of nitrous acid, Figure 2. Kinetic studies of solvolysis of the adducts derived from hemimellitene reveal the characteristics of E1 eliminations. Rates of solvolysis of both the cis and trans-isomers can be correlated to measures of solvent ionizing power such as Grunwald-Winstein Y values, Figure 4. Both isomers give quantitative yields of 4-acetoxyhemimellitene under these reaction conditions; the trans-isomer solvolyzes about four times faster than the cis-isomer throughout the solvent range. The isotope effect in solvolysis is small, $k_H/k_D = 1.2$. Common ion rate depression is observed and concomittant with rate depression one finds a modest increase in the kinetic isotope effect as shown in Figure 5.

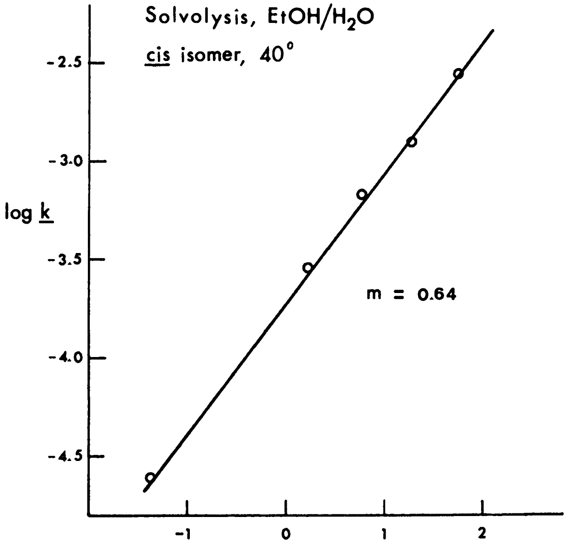


Figure 4. Correlation of solvolysis rate with the Y parameter

A number of anticipated kinetic complications arise as return to reactant or isomeric diene becomes more important. These features will not be dealt with here. Two points of importance should be stressed however. First, the formation of an ipso adduct may give rise to either nitro group rearrangement

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

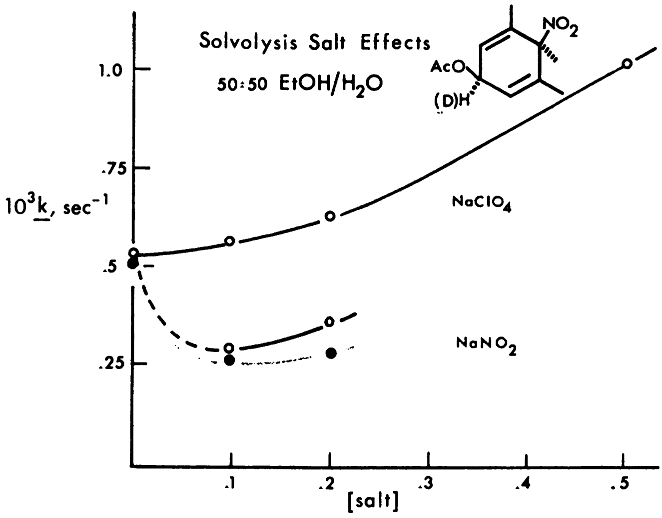


Figure 5. Solvolysis salt effects and istope effects

or the formation of phenolic product; the partitioning depends upon the nucleophilicity of the solvent system used in nitration and/or the method used to process and isolate nitration products. Thus the nature as well as the distribution of products obtained in mononitration of some aromatic systems may vary dramatically with reaction conditions and methods of isolation. Second, some *ipso* ions that are trapped as 1,4-adducts are easily isolated and prove to be fairly stable. These adducts have considerable synthetic potential that remains to be explored.

Reactions of Ipso Ions with Aromatics. *Ipso* ions may be used as carbon electrophiles in the construction of carbon skeletons. Such syntheses are already known but not so identified. For example, a useful synthesis of biphenyls was developed by Puskas and Fields. (7) The conditions are simple. Treatment of excess *o*-xylene or hemimellitene with 90% nitric acid at -20° to -40° yields up to 40% biphenyl coupling products. Cross coupling products with hydrocarbons such as mesitylene could also be obtained in moderate yield. A reasonable interpretation of this result starts with the *ipso* ion. Such an interpretation can be tested by use of isolated 1,4-adducts. Regeneration of the *ipso* ions by treatment with one equivalent of boron trifluoride etherate in excess aromatic hydrocarbon affords biphenyl product in yields up to 70%, Figure 6.

It should be noted that this result lends support to the fundamental assumption of stepwise addition of acetyl nitrate to yield 1,4-adducts. Further, the occurrence of dimerization is

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

one indicator of the life length of ipso ions. The bimolecular reaction competes effectively with intramolecular nitro group shifts.

Coupling (cf. Puskas & Fields, J Org Chem, 32, 3926 (1967))

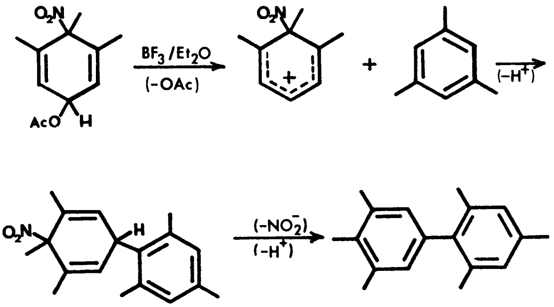


Figure 6. Coupling via ipso *ion*

Scope of the Ipso Phenomenon

A methyl group activates the ipso position in aromatic nitration. This conclusion may be reached in several ways. Perhaps the most straightforward way is to use the reported value of ca. 3% phenyl acetate formed in mononitration of toluene by acetyl nitrate in acetic anhydride and, together with the nitration isomer distribution data, compute the probability of electrophilic attack by the nitrating reagent at various ring positions. (8) The assumption is that each ipso event is successfully diverted via quenching and subsequent elimination of nitrous acid to yield phenyl acetate. With the use of recent rate data of Hartshorn (9), we estimate partial rate factors in toluene to be as shown in Figure 7. Similar conclusions were arrived at independently by Fischer and Wright. (10)

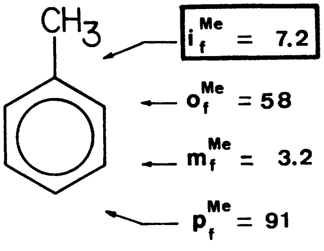


Figure 7. Partial rate factors in nitration

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch004

It should be noted that one can adequately estimate the extent of *ipso* attack in a number of di- and polymethylbenzenes with the use of the partial rate factors shown in Figure 7 and the additivity principle. This measure of internal consistency is reassuring. Moreover, the estimates reveal that *ipso* attack will be significant with the obvious exception of 1,3- and 1,3,5-substitution patterns.

The apparent activation of the *ipso* position by a methyl group is central to the phenomenon of *ipso* substitution, but the result seems difficult to explain within the normal framework of physical organic concepts. That is, modeling the transition state as a developing cyclohexadienyl cation does not suffice to explain the activating effects of methyl, nor can one resort to the other limit, the unperturbed aromatic hydrocarbon. Detailed calculations indicate significantly less electron density at the *ipso* carbon of toluene than at other sites. (11,12) More refined treatments will no doubt yield suitable explanations but it would appear that the rationale developed to account for the extent of *ipso* substitution will differ significantly from those qualitative arguments traditionally used to explain directive effects of substituents in electrophilic aromatic substitution.

An adequate account of the *ipso* phenomenon will also require continued experimental study.

Literature Cited

(1) C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, **93**, 3389 (1971).

(2) P. C. Myhre, *J. Amer. Chem. Soc.*, **94**, 7921 (1972).

(3) R. C. Hahn and M. B. Groen, *J. Amer. Chem. Soc.*, **95**, 6128 (1973).

(4) A. Fischer and J. N. Ramsey, *J. Chem. Soc.*, Perkin II, 237 (1973).

(5) S. R. Hartshorn, *Chem. Soc. Rev.*, **3**, 167 (1974).

(6) D. J. Blackstock, J. R. Cretney, A. Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Lett.*, 2793 (1970).

(7) I. Puskas and E. K. Fields, *J. Org. Chem.*, **32**, 3926 (1967).

(8) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge Univ. Press, London, 1971, p 90.

(9) S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 1256 (1971).

(10) A. Fischer and G. J. Wright, *Aust. J. Chem.*, **27**, 217 (1974).

(11) W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 1496 (1972).

(12) L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, **96**, 137 (1974).

5

Some Recent Developments in *Ipso* Nitration

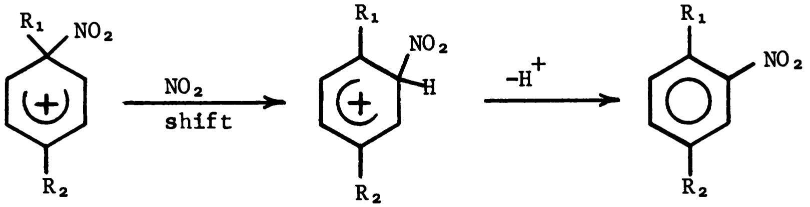
ROGER C. HAHN, HIDETO SHOSENJI, and DAVID L. STRACK

Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

The recent realization that *ipso* (1) electrophilic attack is significant for a number of arenes, (2) some of them commercially important, has opened the door to a new area of exploration, particularly for the organic chemist. The work to be described here is intended to give a glimpse of the potential existing for mechanistic and synthetic studies in this area.

In particular, di- and polyalkylbenzenes having alkyl groups *ortho* or *para* to each other, so that mutual activation toward *electrophilic* attack can occur, may undergo from 25% to as much as 80% ipso attack in nitration reactions. (2,3) As pointed out by Professor Myhre, the *ipso* nitroarenium ions thus formed can undergo a variety of further processes depending on the nature of the substrate and reaction conditions. (4) One of these reactions is shown below.

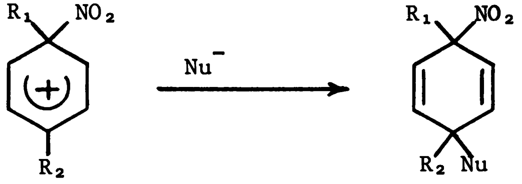


1

In the absence of a trapping nucleophile, 1 can undergo a nitro shift to allow ultimate formation of a "normal" nitrodeprotonation product. (5) For nitrations in non-trapping media, this pathway cannot be distinguished from direct nitrodeprotonation. It becomes necessary, therefore, to determine the extent and consequences of *ipso* attack before true positional selectivities can be established for this type of substrate.

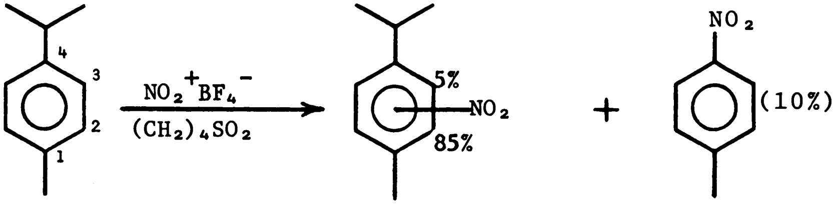
In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

The accumulating weight of indirect evidence indicates that initial positional selectivity of most nitrating agents is nearly the same in a variety of media. (5) One approach to measuring the extent of *ipso* attack (in nitration), then, is to perform the nitration in nucleophilic medium; under these conditions, the *ipso* nitroarenium ion is trapped by *para* nucleophilic addition (below). The amount of 1,4-diene formed is taken to represent the *minimum* amount of *ipso* attack occurring. Diene can be assayed



conveniently by pmr analysis.

We began to look for substrates for which *ipso* attack was likely, but which had not been fully explored. A promising example, *p*-cymene, was found in one of the many pioneering nitration studies by Professor Olah. In 1964, Olah and Kuhn reported (6) that NO_2^+ BF_4^- nitration of *p*-cymene (in sulfolane, a non-nucleophilic medium) gave the product distribution shown below. Form-

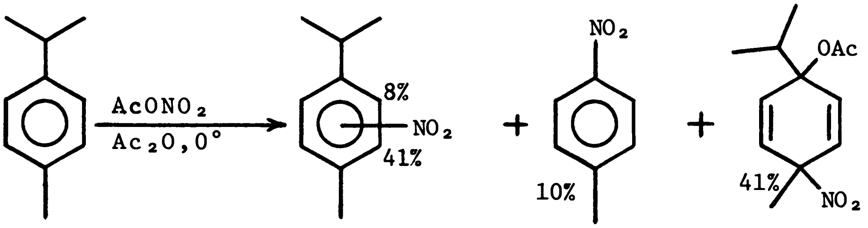


ation of *p*-nitrotoluene was shown at that time to arise from *ipso* attack at C-4, but attack at C-1 also seemed likely to us, in light of more recent work. Since nitrodemethylation is very difficult, a nitro group initially attached at C-1 could simply migrate to C-2; subsequent deprotonation would give a normal-appearing product.

When *p*-cymene was nitrated in the nucleophilic system $AcONO_2/Ac_2O$, the product distribution was indeed different (below). (3c) Subjection of the dienes to strong acid solvolysis gave exclusively 2-nitro-*p*-cymene; the total of 82% 2-nitro isomer thus obtained (41% direct + 41% *ipso* and solvolytic shift) nearly matched the 85% reported for $NO_2^+BF_4^-$ nitration. These results indicate that the previously unsuspected methyl position actually is the most reactive position toward nitration in *p*-cymene. It was noted also that nitrodeisopropylation could not be avoided in Ac_2O; no evidence was found for existence of a species contain-

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

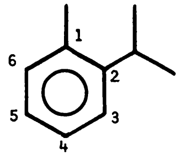


ing geminal nitro and isopropyl groups.

The ortho isomer of cymene next attracted our attention; the extensive study by Olah and Kuhn reported 41% nitrodeisopropylation of this substrate by NO$_2^+$BF$_4^-$. We nitrated o-cymene both with AcONO$_2$/Ac$_2$O and HNO$_3$/H$_2$SO$_4$; results from all three media are assembled in Table I. The differences in detected ipso attack still are under study, and will not be discussed further here. Of more immediate interest was the nature of the ipso dienes formed in AcONO$_2$ nitration, and their subsequent behavior.

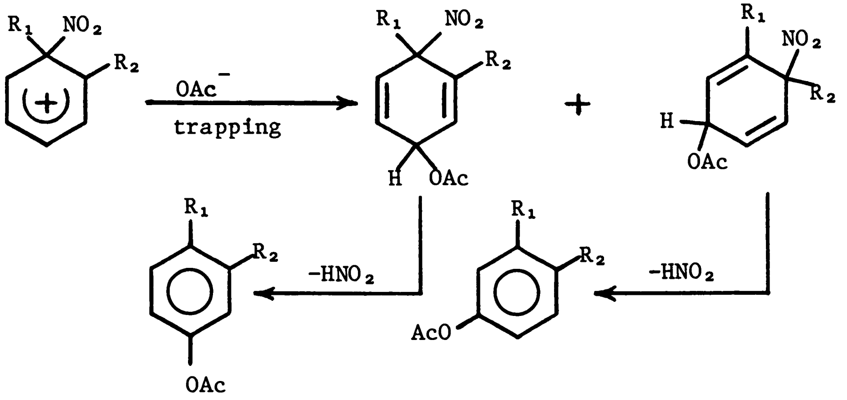
Table I. Nitration of o-Cymene with Various Agents

Agent	3-NO$_2$	6-NO$_2$	Ipso[a]
NO$_2^+$BF$_4^-$ (b)	0.5	11	40.5
HNO$_3$/H$_2$SO$_4$(c)	3	13	15
AcONO$_2$	2	15	22



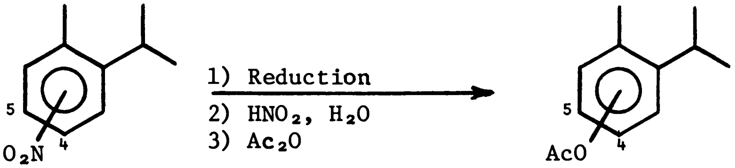
[a]Detectable only; i.e., deisopropylation or adducts. [b]Olah and Kuhn (Ref. 6). [c]This work.

For nitration of many o-dialkylbenzenes in Ac$_2$O, normal workup allows the reaction sequences shown. Thus when R$_1 \neq$ R$_2$,

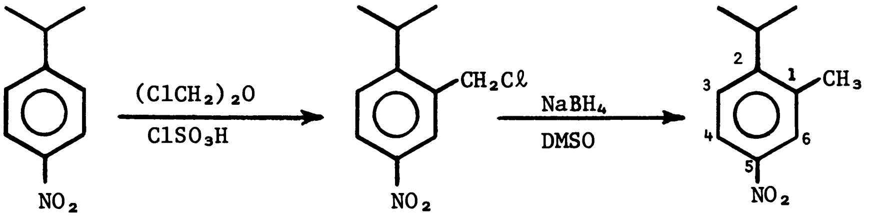


Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

two different acetates can be expected; their relative amounts may give an indication of electrophile distribution between the two *ipso* positions. For *o*-cymene, vpc analysis of the product mixture showed the presence of two acetates in 12:2 ratio. Their structures were linked with the corresponding nitro compounds by the sequence indicated below. However, spectroscopic analyses (pmr,ir) did not afford clearcut evidence of which nitro compound

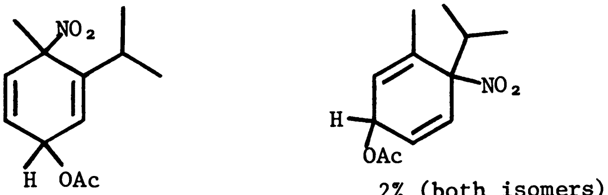


was which. Conveniently for us, Professor A. Mannschreck has independently synthesized 5-nitro-*o*-cymene as follows. (*7*) A



pmr spectrum from his laboratory provided the correlation which allowed assignment of 4-acetoxy-*p*-cymene as the major product (*i.e.*, the one derived from *ipso* attack at the methyl position).

Isolation of the four isomeric *o*-cymene 1,4-nitro, acetoxy adducts (below) also was accomplished (column chromatography), but they could not be separated from one another. Use of Eu(fod)$_3$

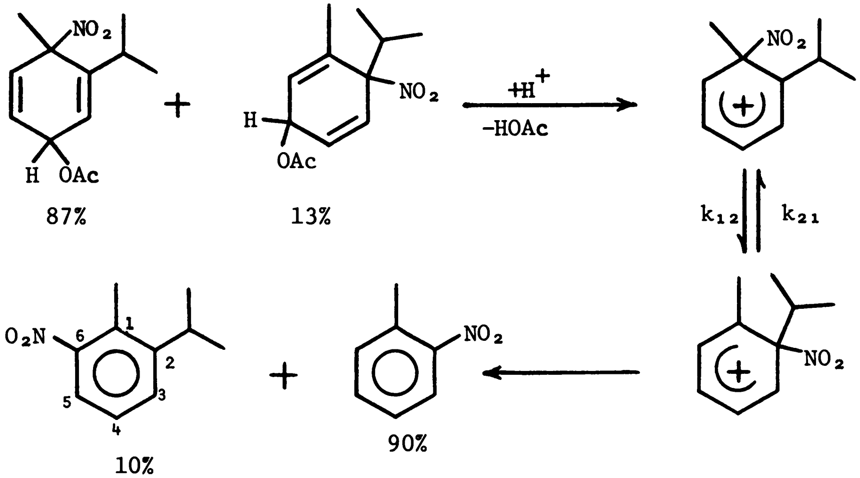


12% (both isomers)

2% (both isomers)

shift reagent on the mixture allowed observation of four distinct acetoxy methyl singlets and isopropyl methyl doublets in the pmr spectra; integration indicated an 87:13 ratio of regioisomers, in satisfactory agreement with the ratio of acetates obtained on work-up and vpc analysis. Thus it was established that the isopropyl group in *o*-cymene is not unavoidably expelled on attachment of a geminal nitro group, in apparent contrast with the behavior of *p*-cymene. The greater stability of the *ortho*-derived system is attributed to the strain introduced on making vicinal methyl and nitro groups coplanar during deisopropylation.

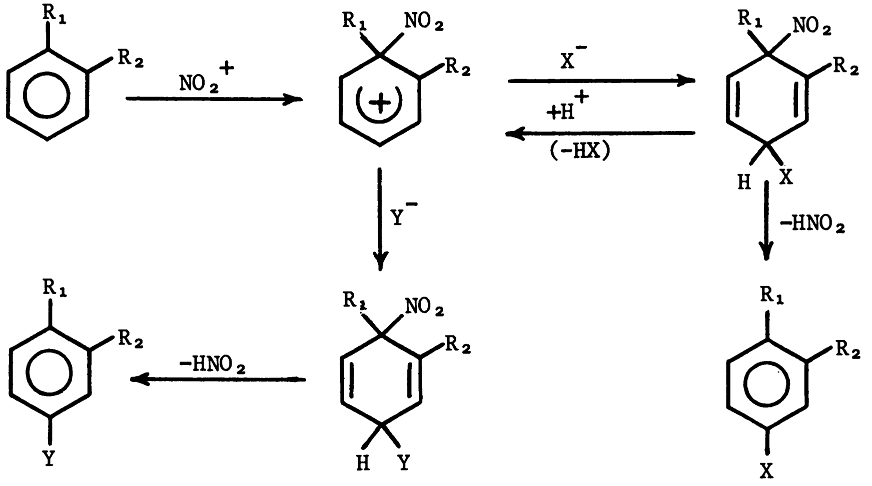
Questions remained concerning the behavior of the two distinct nitroarenium ions derived from attachment of nitro at C-1, and C-2, respectively. Strong acid solvolysis of the mixture of *ipso* adducts gave the results shown below. Two major facts were noted, and corresponding conclusions were reached. First, the



principal product is *o*-nitrotoluene, even though the major adducts had geminal nitro and methyl groups; therefore *ipso*-*ipso* nitro migration (and subsequent deisopropylation) is much more facile in this system than is nitro migration to an unblocked position. Thus one can infer the unusual situation, in $NO_2^+BF_4^-$ or HNO_3/H_2SO_4 nitration of *o*-cymene, of having *ipso* attack at the methyl position masquerading as *ipso* attack at the isopropyl position. Second, the absence of discernible amounts of 3-nitro-*o*-cymene (<1% would have been detected) indicates that nitrodeisopropylation effectively precludes nitro migration to C-3. Hence, the small amount (2%) of 3-nitro derivative from nitration of *o*-cymene must arise only from direct nitrodeprotonation. On the other hand, there is a small but measurable contribution from the "*ipso* route" to formation of 6-nitro-*o*-cymene. The further question of how differently each of the two regioisomeric nitroarenium ions behaves must await separation of *ipso* adduct positional isomers, and is under study.

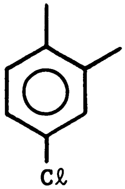
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

Discussion so far has focused on reaction mechanisms. Possible synthetic applications of ipso nitroarenium ions also are being explored; one facet of this work is outlined below.



As described previously for o-cymene, the sequence ipso attack, acetate trapping, and HNO_2 elimination affords aryl acetates; thus an initially electrophilic process culminates in net replacement of hydrogen by a nucleophile. The literature, notably some thorough studies by Professor A. Fischer, (3d,4d) contains examples of replacement of acetate (starting from an ortho- or para-derived ipso adduct) by a variety of oxygen nucleophiles (e.g., OR, ONO_2, O_2CCF_3, O_2CH). However, aromatization of all of these dienes affords only phenol derivatives; we sought to broaden the scope of this process by having the bonding atom in Y some element other than oxygen.

Preliminary work in this area has been with the very stable nitro, acetoxy ipso adducts derived from o-xylene; the first objective was 4-chloro-o-xylene. This simple substance, of interest as an intermediate in the synthesis of riboflavin, is diffi-

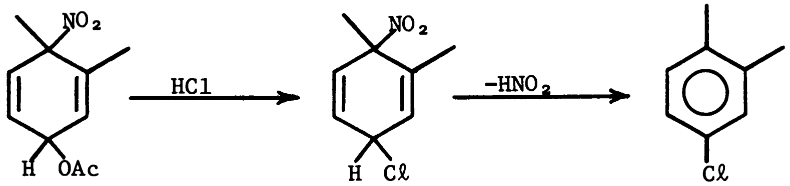


4-chloro-o-xylene

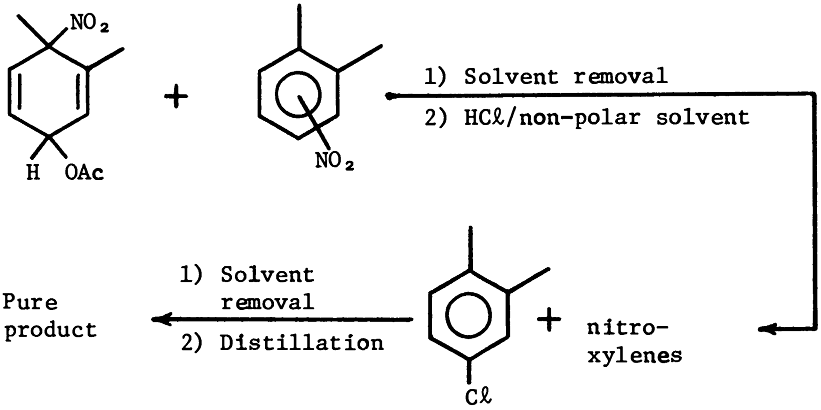
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

cult to obtain pure by classical methods. (8) Direct chlorination of *o*-xylene gives a difficulty separable mixture of isomers, and nitration of *o*-xylene must be followed by fractionation-reduction-Sandmeyer to give the pure 4-chloro derivative. A potential advantage of the *ipso* adduct approach is that only 1,4-adducts appear to form, leading to pure 4-Y derivatives. When a mixture of stereoisomeric *o*-xylene nitro, acetoxy adducts was exposed to dry HCl in nonpolar media, the reaction sequence shown



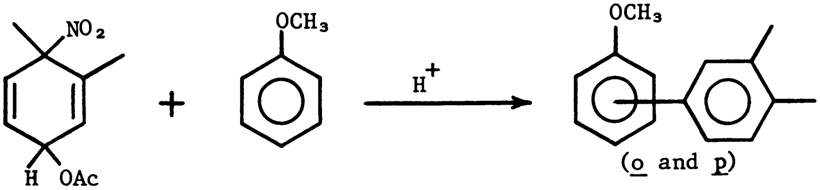
below took place. Further experiments showed that a one-pot synthesis of 4-chloro-*o*-xylene was possible from the hydrocarbon, starting with $AcONO_2$ nitration (below). *Ipso* adducts comprise over 50% of the mixture; the nitro derivatives do not interfere, are separated easily in the final distillation, and remain available for other uses. In general, combination of the *ipso* adduct route with the classical nitration-reduction-Sandmeyer method to prepare 3- or 4-Y-*o*-dialkylbenzenes adds versatility to these syntheses. Thus the *ipso* portion of the initial nitroarenium ion distribution can be diverted at will to a 3-Y derivative (nitration in non-trapping medium, and classical sequence) or to a 4-Y derivative *via* the *ipso* adducts. Introduction of other Y groups is under active study.



One other synthetic application of *ipso* nitroarenium ions can be mentioned. When the mixture of stereoisomeric *o*-xylene nitro, acetoxy adducts was dissolved in anisole and H_2SO_4 was added,

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch005

good yields of the indicated biphenyls were obtained. Clearly,



sufficiently nucleophilic carbon can be included in the Y groups capable of trapping *ipso* nitroarenium ions. The potential of this "custom coupling" process as a route to a variety of biaryls is being further explored. (9)

Acknowledgment. Partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Literature Cited

(1) Perrin, C. L. and Skinner, G. A., *J. Amer. Chem. Soc.*, (1971) **93**, 3389.

(2) *Cf.* (a) Fischer, A. and Ramsay, J. N., *J. Chem. Soc., Perkin Trans.* (1973) **2**, 237; (b) Fischer, A. and Wilkinson, A. L., *Can. J. Chem.*, (1972) **50**, 3988; (c) Fischer, A. and Leonard, D. R. A., *ibid.*, (1972) **50**, 3367; (d) Fischer, A., Greig, C. C., Wilkinson, A. L. and Leonard, D. R. A., *ibid.*, (1972) **50**, 2211.

(3) *Cf.* (a) Fischer, A., Vaughan, J. and Wright, G. J., *J. Chem. Soc. B*, (1967) 368; (b) Blackstock, D. J., Cretney, J. R., Fischer, A., Hartshorn, M. P., Richards, K. E., Vaughan, J. and Wright, G. J., Tetrahedron Lett., (1970) 2793; (c) Hahn, R. C. and Strack, D. L., *J. Amer. Chem. Soc.*, (1974) **96**, 4335; (d) Fischer, A., and Ramsay, J. N., *Can. J. Chem.*, (1974) **52**, 3960.

(4) (a) Blackstock, D. J., Fischer, A., Richards, K. E., and Wright, G. J., *Aust. J. Chem.*, (1973) **26**, 775; (b) Hartshorn, S. R. and Schofield, K., in *Progress in Organic Chemistry*, Vol. 8, W. Carruthers and J. K. Sutherland, Eds., Butterworth and Co., Ltd., London, 1973, p. 278; (c) Hartshorn, S. R., *Chem. Soc. Rev.*, (1974) **3**, 167; (d) Fischer, A. and Ramsay, J. N., *J. Amer. Chem. Soc.*, (1974) **96**, 1614.

(5) (a) Myhre, P. C., *J. Amer. Chem. Soc.*, (1972) **94**, 7921
(b) Hahn, R. C. and Groen, M. B., *ibid.*, (1973) **95**, 6128;
(c) Galley, M. W. and Hahn, R. C., *ibid.*, (1974) **96**, 4337.

(6) Olah, G. A. and Kuhn, S. J., *J. Amer. Chem. Soc.*, (1964) **86**, 1067.

(7) Mannschreck, A., and Ernst, L., *Chem. Ber.*, (1971) **104**, 228.

(8) See Miller, B., *J. Org. Chem.*, (1973) **38**, 1243 and references therein.

(9) Professor Myhre also is making significant contributions in this area; see Ch. (4), this book.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

6

The Reaction of Aromatic Amines with Nitronium Hexafluorophosphate in Nitromethane

T. YOSHIDA

Department of Reaction Chemistry, Faculty of Engineering, Tokyo University,
Hongo, Bunkyo-Ku, Japan

J. H. RIDD

Department of Chemistry, University College, London, 20 Gordon Street,
London WC1, England

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

The reaction of many aromatic amines with nitric acid in concentrated sulphuric acid is well known to give C-nitro products but whether this is a direct C-substitution or an N-substitution followed by rearrangement is usually unknown. The currently accepted view (1) appears to be that nitramine intermediates are seldom involved: this conclusion is based on the marked difference in the product compositions obtained in the nitration of aniline and the rearrangement of phenylnitramine when both reactions are carried out in 85% sulphuric acid (2).

However this is not a valid argument against the reaction of amine molecules through N-substitution followed by rearrangement since aniline under the above conditions undergoes nitration via the conjugate acid (3). At present there is no evidence in the literature against the hypothesis that *all* C-nitrations of amine molecules are N-nitrations followed by rearrangement.

Some evidence for this interpretation (the Bamberger Hypothesis) has been obtained recently: the reaction of 2,3-dinitro-aniline with nitric acid in concentrated sulphuric acid to yield a mixture of the 2,3,4- and 2,3,6-trinitroproducts has been shown to occur through N-nitration followed by a fast rearrangement (4). However, it could be argued that the preferential N-nitration in this molecule is a consequence of the strong deactivation of the aromatic ring by the two nitro substituents: this molecule is not therefore a suitable guide to the nitration of the more reactive aromatic amines.

The difficulty of extending these studies on the Bamberger Hypothesis to the nitration of the more reactive amines in concentrated sulphuric acid comes partly from the incursion of reaction through the conjugate acid and partly from the ready acid-catalysed rearrangement of the nitramines. Some studies have been carried out on the nitration of amines such as aniline in concentrations of sulphuric acid below 82% but the analysis of the reaction mixtures has proved difficult because of subsequent reactions of the mono-nitrocompounds and tarry side-products. These complications have led us to look at the nitration of aromatic amines by preformed nitronium salts in organic solvents. The key question is whether reaction occurs first at the nitrogen or at one of the aromatic carbon atoms. Previous work in this field appears limited to studies on aliphatic amines (5) and on heteroaromatic nitrogen compounds (6), (7).

Products. The experiments were carried out at room temperature by adding a solution of the nitronium salt in the organic solvent to a solution of the amine in the same solvent, the weight of the solutes and volumes of solvent in both solutions being known. The concentration of the amine was more than two-fold that of the nitronium salt so that after complete reaction (shown for N-nitration in equation (1)) an excess of the free amine should still be present. This should reduce the acidity of the solution to the point where rearrangement of the nitramine can be ignored.

$$2ArNH_2 + NO_2^+ = ArNHNO_2 + ArNH_3^+ \qquad (1)$$

The preliminary experiments were carried out using both nitronium tetrafluorophosphate in sulpholane and nitronium hexafluorophosphate in nitromethane. However, the products from these experiments had unexpectedly high concentrations of nitroso compounds; this was traced to significant amounts of nitrosonium salts in the supposedly pure nitronium salts. A method was devised for the purification of nitronium hexafluorophosphate (see Experimental) which, from the raman spectra, was completely effective in removing this impurity. The same method did not work well for nitronium tetrafluoroborate and so all subsequent work was carried out using the hexafluorophosphate salt.

The analysis of the reaction products was carried out by integration of the n.m.r. spectra of the material obtained by extraction. The results are listed in Table I. The product composition is given as mole % in terms of the sum of identified products, and the amount of nitronium salt accounted for in this way is also given as a percentage of that initially weighed out. The integrals were converted to percentages of products by comparison with the integral of a weighed amount of trinitrobenzene introduced initially into the reaction and used as a standard. Trinitrobenzene does not react significantly with nitronium salts under these conditions.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

Table I

Product composition for the reactions of aromatic amines with nitronium hexafluorophosphate in nitromethane

Exp.	Substrate and Reaction Conditions	Products(%)[a]	Overall yield(%)[b]
(A)	2,4-dinitroaniline amine, 0.61 g, 5.0 ml NO_2PF_6, 0.19 g, 2.0 ml	N,2,4-trinitro(100)	95
(B)	2,3-dinitroaniline amine, 0.30 g, 4.0 ml NO_2PF_6, 0.2 g, 1.5 ml	N,2,3-trinitro(100)	103
(C)	2,4-dinitro-N-methylaniline amine, 0.35 g, 7.0 ml NO_2PF_6, 0.15 g, 2.0 ml	N-methyl-N,2,4-trinitro (26) N-methyl-2,4,6-trinitro (41) N-methyl-N,2,4,6-tetranitro (33)	85
(D)	2,4-dinitro-N-methylaniline amine, 0.24 g, 8.0 ml NO_2PF_6, 0.11 g, 6.0 ml	N-methyl-N,2,4-trinitro (51) N-methyl-2,4,6-trinitro (42) N-methyl-N,2,4,6-tetranitro (7)	38
(E)	4-nitroaniline amine, 0.50 g, 3.0 ml NO_2PF_6, 0.24 g, 3.0 ml	N,4-dinitro (60) 2,4-dinitro + N,2,4-trinitro (29)[c] $4\text{-}NO_2C_6H_4\overset{+}{N}_2$ (11)	80
(F)	4-nitroaniline amine, 0.48 g, 2.0 ml NO_2PF_6, 0.11 g, 5.0 ml	N,4-dinitro (66) 2,4-dinitro + N,2,4-trinitro (21)[c] $4\text{-}NO_2C_6H_4\overset{+}{N}_2$ (13)	85
(G)[d]	4-nitroaniline amine, 0.44 g, 4.5 ml NO_2PF_6, 0.25 g, 4.5 ml	N,4-dinitro (83) 2,4-dinitro + N,2,4-trinitro (17)	72

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

Table I (cont.)

Exp.	Substrate and Reaction Conditions	Products(%)[a]	Overall yield(%)[b]
(H)	2-chloro-4-nitro aniline amine, 0.52 g, 5.0 ml NO_2PF_6, 0.24 g, 3.0 ml	2-chloro-N, 4-dinitro (57) 2-chloro-N, 4, 6-trinitro (27) 2-Cl-4-$NO_2C_6H_3\overset{+}{N}_2$ (16)	64
(I)[d]	2-chloro-4-nitro aniline amine, 0.51 g, 4.5 ml NO_2PF_6, 0.25 g, 4.5 ml	2-chloro-N, 4-dinitro (83) 2-chloro-N, 4, 6-trinitro (12) 2-Cl-4-$NO_2C_6H_3\overset{+}{N}_2$ (5)	76
(J)	N-methyl-4-nitro aniline amine, 0.40 g, 1.5 ml NO_2PF_6, 0.13 g, 2.0 ml	N-methyl-N, 4-dinitro (25) N-methyl-N, 2, 4-trinitro (44) N-methyl-N-nitroso-4-nitro (31)	69
(K)	N-methyl-4-chloro aniline amine, 0.33 g, 1.5 ml NO_2PF_6, 0.12 g, 1.5 ml	N-methyl-N-nitro-4-chloro (20) N-methyl-N, 2-dinitro-4-chloro (46) N-methyl-N, 2, 6-trinitro-4-chloro (34)	85
(L)	N, N-dimethyl-4-nitroaniline amine, 0.24 g, 2.0 ml NO_2PF_6, 0.13 g, 1.4 ml	N, N-dimethyl-2, 4-dinitro (100)	79
(M)	N, N-dimethyl-4-chloroaniline amine, 0.33 g, 2.0 ml NO_2PF_6, 0.08 g, 1.5 ml	N, N-dimethyl-2-nitro-4-chloro (100)	110

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

Table I (cont.)

Exp.	Substrate and Reaction Conditions	Products(%)[a]	Overall yield(%)[b]
(N)	N, N-dimethyl-4-methylaniline amine, 0.23 g, 2.0 ml NO_2PF_6, 0.14 g, 1.5 ml	N, N-dimethyl-2-nitro-4-methyl(100)	100
(O)	N-methyl-N, 2, 4-trinitroaniline amine, 0.31 g, 7.0 ml NO_2PF_6, 0.12 g, 5.0 ml	N-methyl-N, 2, 4, 6-tetranitro (34) N-methyl-2, 4, 6-trinitro (63) N-methyl-N-nitroso-2, 4-dinitro(3)	24
(P)	N, 4-dinitroaniline amine, 0.29 g, 2.0 ml NO_2PF_6, 0.14 g, 5.0 ml	N, 2, 4-trinitro (50) 2, 4-dinitro (50)	90

Footnote

[a] Moles % of identified products.

[b] Calculated from the weight of nitronium salt used. For this purpose, the formation of nitroso or diazonium derivatives is assumed to involve one nitronium ion per molecule.

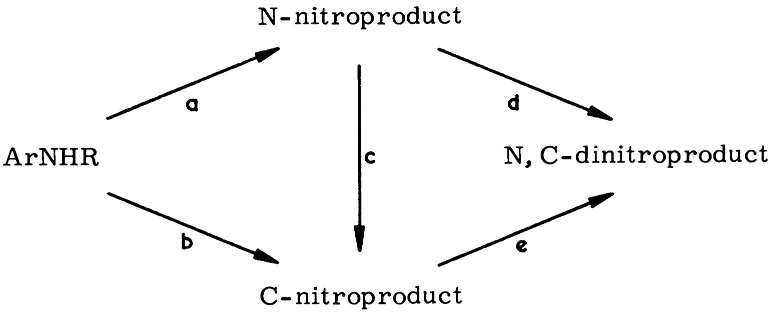
[c] Interference by other peaks in the n. m. r. spectrum prevents the separate estimation of these products.

[d] Preliminary experiments using fast mixing technique (see Experimental).

Discussion

The fact that 2,4-dinitroaniline and 2,3-dinitroaniline react with nitronium hexafluorophosphate in nitromethane to give essentially quantitative yields of the N-nitro compounds (Table I, exp. A, B) is in accord with previous work in other media (4).

The formation of a significant amount of the C-substituted product with 2,4-dinitro-N-methyl aniline is more unexpected (Table I, exp. C) and the possible reaction paths are best discussed in terms of the network in Scheme 1. The C-substituted product could be derived either directly (path b) or via the nitramine (path a and c).



Scheme 1

In deciding this matter, the presence of a large amount of the product of further reaction (N-methyl-N,2,4,6-tetranitroaniline) is significant. Since the amine is in more than two-fold excess, the presence of the disubstituted compound suggests that the reaction is fast in comparison with mixing or solution*. This

---

* The solubility of this substrate is less than that of the other dinitroanilines and some solid amine may have been suspended in the reaction mixture.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

would lead to local regions of enhanced acidity which, in principle could lead to rearrangement of the amine. The addition of the nitronium salt to a solution of the corresponding nitramine in nitromethane brings about this rearrangement (Table I, exp. O), for the reaction mixture contains more of the rearranged nitramine than of the tetranitroproduct. Thus it is plausible that the the C-substituted product is derived largely or completely from paths (a + c). When the concentrations of N-methyl-2,4-dinitroaniline and nitronium hexafluorophosphate are reduced, the yield of the N-nitroproduct exceeds that of the C-nitroproduct (Table I, exp. D) and so the initial substitution appears to be more on nitrogen than on carbon.*

The formation of significant amounts of C-substituted products in the reaction of 4-nitroaniline with nitronium hexafluorophosphate can be explained in the same way (Table I, exp. E). Here there is no doubt that reaction should be fast in comparison with the mixing of the solutions for this amine is known to react on encounter with the nitronium ion (3). This should give rise to regions of enhanced acidity which could lead both to rearrangement of the nitramine and further substitution as illustrated for the reaction of the nitramine itself in exp. P. With 4-nitroaniline, the amount of the N-substituted product exceeds that of the C-substituted product and increases as the reactants are diluted (exp. F) and when the efficiency of mixing is improved (exp. G). The results with 2-chloro-4-nitroaniline are similar (exp. H and I). These experiments suggest that the apparent C-nitrations of 4-nitroaniline and 2-chloro-4-nitroaniline in concentrated sulphuric acid (3) are in fact N-substitutions followed by fast rearrangements.

The amines listed in Table I include also several *para*-substituted N,N-dimethyl compounds. These give good yields of mononitro compounds. Presumably any of the quaternary ion $Ar\overset{+}{N}Me_2NO_2$ formed at once rearranges. Reaction may stop at the mono-nitro stage because the presence of the *ortho*-nitro group decreases the conjugation of the $-NMe_2$ group with the ring and so hinders subsequent reactions during mixing.

---

* The amount of the 2,4,6-trinitro and N,2,4,6-tetranitrocompounds should perhaps be added together in estimating the maximum possible percentage of C-substitution since the latter may be formed from the former. However, the ready reaction of nitronium ions with the N-methyl-N,2,4-trinitroaniline (exp. O) shows that this reaction (path d) is also a route to the tetrasubstituted compound.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

One interesting feature of the results in Table I is the formation of some nitroso or diazonium compounds presumably as a result of oxidation by the nitronium ion rather than substitution. Some of this oxidation may occur during the rearrangement of the of the nitramine. Studies with the more basic primary and secondary amines (e.g. *para*-toluidine and N-methyl-*para*-toluidine) indicate that the pathway leading to oxidation is then far more important: this aspect of the work is being studied further.

Experimental

Materials. 2,3-dinitroaniline (**8**), *p*-methyl-N,N-dimethylaniline (**9**), *p*-chloro-N,N-dimethylaniline (**9**), *p*-nitro-N,N-dimethylaniline (**10**), N-methyl-*p*-toluidine (**11**), *p*-chloro-N-methylaniline (**11**), N,2,4-trinitroaniline (**12**), 2,4-dinitro-N-methylaniline (**13**), 2,4-dinitro-N,N-dimethylaniline (**13**) and N,2,4-trinitro-N-methylaniline (**14**) were prepared by known methods. Spectroscopic grade nitromethane and methylene chloride were dried using a molecular sieve. The other substrates were either available from related studies or were purchased and purified by standard methods.

Nitronium tetrafluoroborate, nitronium hexafluorophosphate and nitrosonium tetrafluoroborate were obtained from Ozark-Mahoning Company.

Purification of Nitronium Hexafluorophosphate. Commercial nitronium hexafluorophosphate (A, 17.7 g) was dissolved in nitromethane (170 ml) and methylene chloride (170 ml) was added. The precipitated salt (B) was filtered and part removed for the determination of its purity. The remaining precipitate was dissolved in nitromethane (150 ml) and methylene chloride (150 ml) added to the solution. The reprecipitated salt (C, 2.8 g) was filtered and dried under vacuum in a desiccator over phosphorous pentoxide. All operations with nitronium salts were carried out in a dry box.

The purity of these samples was estimated from the Raman spectra and from the yields of 2,4-dinitrotoluene obtained from the salts. *p*-Nitrotoluene reacts readily with nitronium salts to give a quantitative yield of 2,4-dinitrotoluene, but does not react with nitrosonium salts at room temperature. The purified nitronium salt (C, 0.254 g) was dissolved in nitromethane (3 ml) and added dropwise to a solution of *p*-nitrotoluene (0.402 g) in 2 ml of the same solvent. After fifteen minutes the reaction

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

mixture was poured into ether (50 ml). The solution was washed twice with water, dried on magnesium sulphate, and filtered. After evaporation of the solvent, the residue was dissolved in deuterated chloroform and analysed by n. m. r. The yield of 2, 4-dinitrotoluene, based on the amount of nitronium salt used, was calculated from the relative areas of the methyl proton peaks of the product and the substrate. The results of such analyses on samples (A), (B) and (C) are shown in Table II.

Table II

Purity of the samples of nitronium hexafluorophosphate

Sample	Raman line of NO^+ ($2329\ cm^{-1}$)	Yield in nitration of p-nitrotoluene
A	strong	76%
B	trace	97%
C	absent	100%

Products. The product analyses for the reaction of nitronium hexafluorophosphate with aromatic amines were carried out by n. m. r. A solution of the nitronium salt and trinitrobenzene (as a standard material for n. m. r. analysis) in nitromethane was added dropwise, with shaking, to a solution of an amine in the same solvent. After fifteen minutes the reaction mixture was poured into ether (50 ml), and any precipitate filtered off using a glass filter. The precipitate was dissolved in a small amount of acetone and analysed for the diazonium salt by n. m. r. The ether solution was washed with water, dried on magnesium sulphate and filtered using a filter paper. After evaporation of the solvent under reduced pressure, the products were dissolved in acetone or deuterated chloroform and analysed by n. m. r.

Rapid mixing experiment. A mixing device (Union Giken Co., Model MX-7) was used for rapid mixing experiments. In these experiments, the substrates and the nitronium salt were weighed and dissolved in separate samples (4. 5 ml) of dry nitromethane. The latter solution contained known amount of trinitrobenzene as standard. These solutions were placed in two reservoirs of the apparatus which was in turn placed in a dry box containing phosphorous pentoxide. Samples (0. 25 ml) of each of the solutions were withdrawn from the reservoirs into each of two syringes,

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

and then ejected through a four jet mixer into a flask. This operation was repeated until almost all of the stock solutions were exhausted. The reaction mixture was treated as before and analysed for products.

We thank Ira Hollinshead and Mr. D. J. Mills for supplying some of the amines used and Mr. T. Andoh for assistance with some of the experimental work.

Abstract

The reaction of some dinitroanilines (in excess) with nitronium hexafluorophosphate in nitromethane leads to essentially complete N-substitution but, with more basic amines, the product composition includes C-substituted and polysubstituted material. Evidence is presented to suggest that the C-substitution is derived, at least in part, from N-substitution followed by rearrangement in local regions of high acidity generated during reaction. This argument is supported by studies on the reactions of the related N-nitro compounds with nitronium ions. The results support Bamberger's view that the nitration of aromatic amines occurs initially at the amino nitrogen atom.

Literature Cited

(1) White, W. N., "Mechanisms of Molecular Migrations", ed. B. S.,Thyagarajan, vol. 3, p. 109, see esp. p. 114, Wiley, New York, 1971.
(2) Hughes, E. D. and Jones, G. T., J. Chem. Soc., (1950), 2678.
(3) Hartshorn, S. R. and Ridd, J. H., J. Chem. Soc., (1968), 1063, 1068.
(4) Ridd, J. H. and Scriven, E. F. V., J. C. S. Chem. Comm., (1972), 641.
(5) Olsen, R. E., Fish, D. W. and Hamel, E. E., "Advances in Propellant Chemistry" Adv. Chem. Series, (1966), 54, 48.
(6) Olah, G. A., Olah, J. A. and Overchuk, N. A., J. Org. Chem., (1965), 30, 3373.
(7) Jones, J and Jones, J., Tetrahedron Letters, (1964), 2117.
(8) Kremer, C. B. and Bendich, A., J. Am. Chem. Soc., (1939), 61, 2658.
(9) Thomas, D. G., Billman, J. H. and Davis, C. E., J. Am. Chem. Soc., (1946), 68, 895.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

(10) Cambell, T. W., J. Am. Chem. Soc., (1949), 71, 740.

(11) Roberts, R. M. and Vogt, P. G., Organic Synthesis, Coll. (1963), vol. 4, 420.

(12) Glazer, J, Hughes, E. D., Ingold, C. K., James, A. T., Jones, G. T. and Roberts, E., J. Chem. Soc., (1950), 2657.

(13) Hodgson, H. H. and Turner, G, J. Chem. Soc., (1942), 584.

(14) Clarkson, C. E., Holden, I. G. and Malkin, T., J. Chem. Soc., (1950), 1556.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch006

7

Nitration and Oxidative Side Reactions of Dinitrotoluenes

DAVID S. ROSS and NORMAN A. KIRSHEN
Stanford Research Institute, Menlo Park, Calif. 94025

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Introduction

Aromatic nitration has been studied in great detail for several decades, and as a result, it stands as one of the relatively few well understood phenomena in organic chemistry. However, the oxidation processes that accompany nitration in most cases are little understood. In particular, in cases of the nitration of severely deactivated aromatic compounds, where conditions of strong acid and high temperatures must be employed, (1) the oxidation of substrate can be a significant, undesirable side reaction. At worst, in the case of 3,5-dinitrotoluene, for example, oxidation is the reported sole mode of reaction (2).

This account deals with our studies of the oxidation of dinitrotoluenes (DNT) in mixed nitric/sulfuric media with acidities ranging from 85% H_2SO_4 to oleum systems. Our goal was the identification of the oxidizing species in the system and the development of some insight into the oxidation mechanism.

Background

A number of studies of oxidation in nitric acid media are in the literature. Titov has reported on his extensive studies of alkyl aromatic oxidation in aqueous anhydrous nitric acid.(3) He found that in anhydrous nitric acid or in the more concentrated aqueous nitric acids, and at temperatures above about 280°C, NO_3 is the effective oxidizer.

$$NO_3 + RH \longrightarrow R + HNO_3$$

In aqueous nitric acid at lower temperatures, he reported no reaction in the absence of NO or NO_2 and concluded that NO_2 is

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

the active oxidizer in these systems, generated autocatalytically in the sequence

$$NO_2 + RH \longrightarrow R\cdot + HNO_2 \qquad (1)$$

$$HNO_2 \longrightarrow 1/2\ H_2O + 1/2\ NO + 1/2\ NO_2 \qquad (2)$$

$$1/2\ NO + HNO_3 \longrightarrow 3/2\ NO_2 + 1/2\ H_2O \qquad (3)$$

The overall reaction is

$$RH + HNO_2 \longrightarrow NO_2 + H_2O + R\cdot \qquad (4)$$

with the net production of one NO_2 per cycle.

Longstaff and Singer studied the oxidation of formic acid in both nitric acid and mixtures of nitric and other mineral acids at 25°, and found that no oxidation took place in the absence of N(III) (HNO_2 or NO^+).* (4) They observed autocatalysis and acid catalysis and proposed that NO^+ was the effective oxidizer in the system. Their scheme (simplified here) was

$$NO^+ + e^- \longrightarrow NO \qquad (5)$$

$$3/2\ H^+ + NO + 1/2\ HNO_3 \longrightarrow 3/2\ NO^+ + H_2O \qquad (6)$$

in which the NO^+ is increased by 50% each cycle.

Autocatalytic behavior is a common observation in nitric acid oxidations of various substrates in mixed acids, (5, 6) and generally the catalyst has been found to be nitrous acid. Acid catalysis, or an increase in oxidation rate over at least some portion of the acidity ranges studied, is also commonly observed, and the oxidizing species NO_2, N_2O_4, and HNO_2^+ have been proposed by various authors.

---

*Since the forms of the oxidation states of the oxy-acids of nitrogen to be dealt with here vary with the acidities of the media employed, it is convenient in discussion to refer to the oxidation states themselves. Thus, as is discussed in the text below, N(III) can be nitrite ion, nitrous acid, or nitrosonium ion (NO^+), and N(V) can be nitrate ion, nitric acid, or nitronium ion.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Only limited studies of oxidations in the highly acidic media useful in aromatic nitrations of deactivated systems have been reported. Bennett et al. found that in the nitration of 2,4-dinitrotoluene the major products of oxidation were CO, CO_2, and nitrous acid. (7) While the degree of oxidation was low in these laboratory experiments at low conversions, in largescale operations such as the manufacture of TNT, oxidation has been found to lead to significant reduction in yields, to problems of product purification, and to the production of relatively large quantities of noxious, volatile materials, including NO_x and tetranitromethane. (8)

Holahan et al. (9) studied the oxidation of several dinitrotoluenes under nitration conditions and reported that the relative rates of oxidation are in a direct inverse relationship to their rates of nitration. Our data will deal with these results.

The various species present in nitration media of different acidities are presented in Figure 1. The forms of the oxy-acids of the N(III) and N(V) oxidation states of nitrogen are shown as a function of acidity; also shown is the point of significant protonation of 2,4-DNT. The scale used at the bottom of the figure is the Hammett acidity function, used here for convenience, since the function spreads the acid regions of interest, even though the species involved are not necessarily Hammett bases.

As the figure shows, below about 50% sulfuric acid, N(III) is present in the solution as nitrous acid. With increasing acidity, nitrosonium ion (NO^+) begins to become important, and finally at 65% sulfuric acid, the species is essentially completely converted.

The N(V) species display a behavior similar to that of N(III), but shifted toward higher acidities. Thus, molecular nitric acid is the predominant species from 60% to about 75% sulfuric acid. At that point nitronium ion (NO_2^+) begins to become important, and at 90% acid, the conversion is essentially complete. (Note that since nitric acid is a considerably stronger acid than nitrous acid, nitrate is seen in 20% sulfuric acid, whereas nitrous acid is present down to below $-H_0 = 0$.)

Finally, it can be seen that 2,4-DNT is not significantly protonated below about 25% oleum.

These data are derived from spectroscopic studies and apply to quantities of solute in the range 10^{-2} to 10^{-4} M. At the much higher nitric acid concentrations used in nitration work, molecular nitric acid can be present in oleum solutions, for example, in significant concentrations. (10) Thus, at high

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

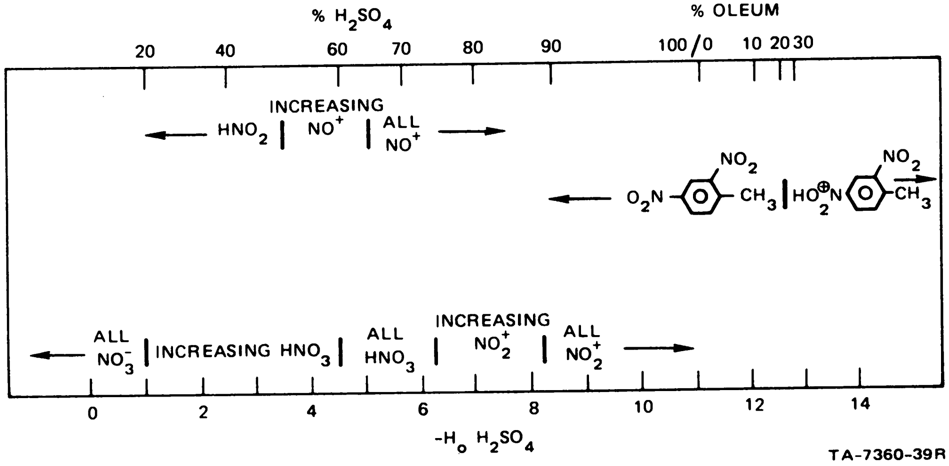


Figure 1. The nature of various species involved in DNT nitration with changing acidity

References: HNO_2, N. Bayliss et al., Aust. J. Chem. 16, 933 (1963); DNT, J. Brand, W. Horning, and M. Thornley, J. Chem. Soc., 1374 (1952); HNO_3, N. C. Deno, H. Peterson, and E. Sacher, J. Phys. Chem.., 65, 199 (1961).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

solute levels, while the gross positions of the equilibria shown in Figure 1 may not be greatly different, substantial changes occur in the relative quantities of materials at a given acidity. These changes are undoubtedly due to large medium effects at such high solute concentrations.

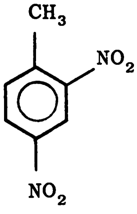
Results

Survey Studies

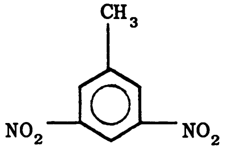
We began our study with a general survey of the chemistry of the system. The term "oxidation" used in the text actually refers to the unaccounted-for organic material in any given experiment. Thus, $DNT_{ox} = DNT_o - (DNT_f + TNT)$, where DNT_{ox} is the quantity of oxidized substrate, DNT_o is the starting quantity, DNT_f is the final DNT quantity, and TNT is the quantity of product trinitrotoluene formed.

Gaseous Products. The oxidation observed in this work ranged from about 5% of the reacted DNT, in the case of the 2,4- and 3,4-isomers, to more than 50%, in the case of 3,5-DNT. The gaseous products and ratios obtained in all runs were $CO:CO_2:C(NO_2)_4 \approx 1:1:10^{-2}$. This ratio remained roughly the same under the large variety of conditions employed, with the exception that in oleum systems no tetranitromethane (TNM) was evolved. The carbon gases comprised about 15-20% of the oxidized substrate. The remaining organic material was water soluble, and attempts at isolation and identification were unsuccessful. Nitrous oxide (N_2O) was also a commonly observed product, formed to about 40% of the CO_2 quantities, and SO_2 was seen in the oleum runs, formed to about half of the CO_2 quantities.

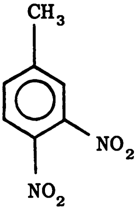
Isomers. Initially both the oxidation and nitration rates of three dinitrotoluene (DNT) isomers were studied. The isomers studied were



2,4-DNT



3,5-DNT



3,4-DNT

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

The results are shown in Table I.

Table I

RATES OF NITRATION AND OXIDATION OF DNT ISOMERS AT 90°[a]

DNT Isomer	Relative Rates	
	k_n[b]	k_{ox}
2,4-DNT	18.1	0.9
3,5-DNT	1.0	1.0
3,4-DNT	29.3	1.4

[a] Reactions carried out in media with the molar ratio $H_2SO_4:HNO_3:DNT = 10:1:0.5$.

[b] Overall nitration.

Somewhat surprisingly, the data show that while the nitration rates for the three isomers vary significantly, the oxidation rate constants are the same to within less than a factor of two. These data are contrary to the conclusions of Holahan et al. (9) that the rates of oxidation of the DNT isomers are inversely related to the nitration rates.

On the basis of our results, we suggest that the oxidation rate constants for all six DNT isomers are about the same. Subsequently, 3,5-DNT was used almost exclusively as an analytical probe into the oxidation, since the "leverage" afforded by its nitration/oxidation ratio was favorable for a study of the oxidation.

The nitration results for the three isomers are discussed in detail in the Appendix.

Effect of Added N(III). As stated above, the reported results for nitric acid oxidations in mixed acids and at lower temperatures and acidities generally noted the observation of autocatalysis by N(III). Under the conditions used in this study, however, N(III) was found to be inactive. In Table II we present the data for experiments in which sodium nitrite,

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Table II

EFFECTS OF O_2, N(III), H_2SO_4, AND SO_3 ON THE OXIDATION OF DNT

Experiment No.	DNT Isomer	Condition	Reaction Time (hr)	Recovered (mmol)[a]			Recovery Yield (%)[b]
				DNT_o	DNT_f	TNT	
1	2,4-DNT	Control	0	8.13	8.08	0	99.3
2		Standard[c]	1	8.03	2.20	5.42	94.9
3		Standard[c]	17	7.98	0	7.19	90.1
4		N_2 (730 torr)	1	8.04	2.99	4.82	97.1
5		O_2 (730 torr)	1	8.03	1.65	5.88	93.9
6		$NaNO_2$ added[d] (NO^+ source)	1	8.08	3.89	3.72	94.2
7		Na_2SO_4 added[e]	1	8.14	2.64	5.02	94.2
8	3,5-DNT	Standard[c]	1	8.24	6.93	0.50	90.2
9		Standard[c]	17	8.05	5.67	1.16	84.9
10		No nitric acid	17	8.08	7.83	0	96.9
11		No nitric acid and 30% Oleum	1	8.15	7.83	0	96.1

[a] DNT_o = starting DNT; DNT_f = final DNT; TNT = product TNT.

[b] Defined as $[DNT_f + TNT)/DNT_o]$ x 100.

[c] Defined as runs in 95% H_2SO_4 with mole ratios H_2SO_4:HNO_3:DNT = 10:1:0.5.

[d] DNT:NO^+ = 1:1:

[e] Sufficient Na_2SO_4 was added to provide an ionic strength identical to that in the $NaNO_2$ runs.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

a suitable source of N(III), has been added to some nitration mixtures. The table also presents data for assessing the effects of O_2, H_2SO_4, and SO_3 on the oxidation rate.

The results for 2,4-DNT show that the presence of N(III) has little effect on the recovery yield. The run under nitrogen seems to have gone somewhat more efficiently than the others; however, no major effects from the presence of oxygen are evident.

The data for 3,5-DNT suggest that sulfuric acid does play a small role in the oxidation. Since the recovery efficiency was 99.3% (Expt. 1), but the recoveries in Runs 10 and 9 are only 96.9% and 84.9%, respectively, for runs without and with nitric acid, the sulfuric acid must be responsible for about 20% of the total loss.

Finally, a comparison of the recovery yield data for sulfuric acid and oleum media (Runs 10 and 11) shows that SO_3, or perhaps more properly $H_2S_2O_7$* has no significant effect.

We conclude that N(III), O_2, H_2SO_4, and SO_3 have at best only secondary effects on the oxidation process. These results are interesting with regard to the cited catalytic effects of N(III). Our results here clearly show that some mechanism other than that proposed in the literature accounts of nitric acid oxidation (4) must be operative in DNT nitration media. This conclusion is reasonable since the acidities in the current work are significantly higher than those used in the literature work.

Kinetic Study of 3,5-DNT

The detailed kinetics of both nitration and oxidation of 3,5-DNT were studied at 60° and 90°.

Stoichiometry and Kinetics. The experiments were run in mixtures with the mole ratios $H_2SO_4:HNO_3:DNT = 10:1:0.5$. A 2:1 ratio of nitric acid to substrate was established initially; however, as in shown in Figure 2, both at 60° and 90° the N(V) concentration (both HNO_3 and NO_2^+) falls much more rapidly than does that of the DNT.

The specific degree of N(V) consumption in the oxidation is shown in Table III, which presents the incremental decline in N(V) observed with time per unit oxidized DNT, along with production of NO^+. [The $\Delta N(V)$ values are corrected for the quantities used in nitration.]

---

*It has been shown that SO_3 dissolved in sulfuric acid readily forms $H_2S_2O_7$ and higher polysulfuric acids. (11)

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

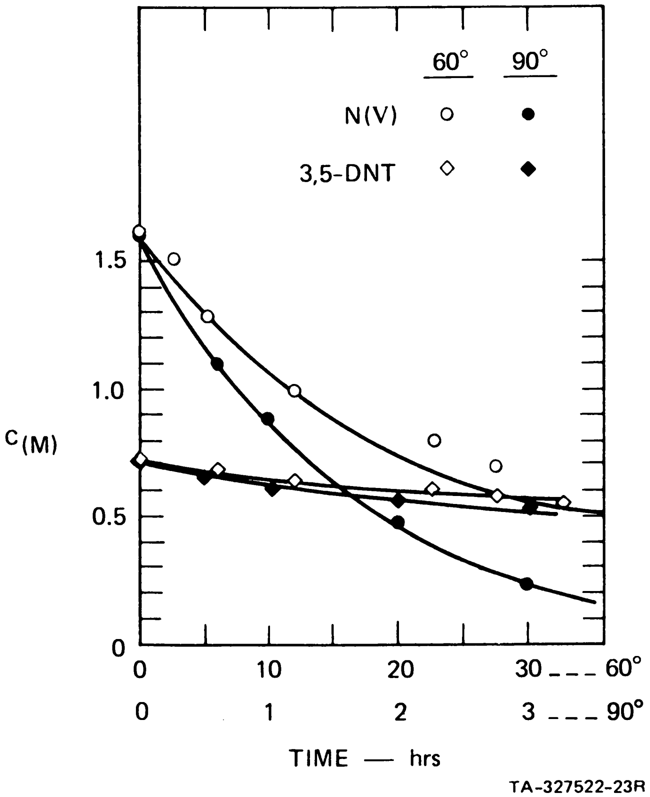


Figure 2. Consumption of N(V) and 3,5-DNT at 60° and 90°

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

There is some scatter in the data; however, it seems clear that about 11 or 12 molecules of N(V) are consumed per molecule of DNT oxidized, with the parallel production of comparable quantities of N(III) or NO^+ at these acidities.

Figure 3 shows a first-order plot of our data at 60° and indicates that the decline in N(V) concentration nicely follows first-order decay to better than two half-lives. The system is really pseudo-first-order, and this result is somewhat unusual because the reactant in excess is the one displaying first-order behavior. The usual case is the other way around, with the reactant in smaller initial concentration showing first-order consumption. (12) The behavior in the current case is, of course, due to the large values of the $\Delta N(V)/DNT_{ox}$ ratio.

Table III

N(V) CONSUMPTION AND NO^+ PRODUCTION PER DNT AT 60° AND 90°

60°			90°[a]	
Time (hr)	$\Delta N(V)/DNT_{ox}$	NO^+/DNT_{ox}	Time (hr)	$\Delta N(V)/DNT_{ox}$
6	16.1	8.7	0.25	4.4
12	9.9	7.5	0.5	10.9
23	11.7	12.1	1	11.4
28	11.0	11.2	2	10.3
33	11.2	9.6	3	11.7
47	12.6	11.4	5	11.6
55	13.0	11.9	--	--
71	12.9	12.4	--	--
	Ave. = 12.3	Ave. = 10.6		Ave. = 11.2[b]

[a] The NO^+ production was not followed in the 90° work.

[b] The 4.4 value was not included in the averaging.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

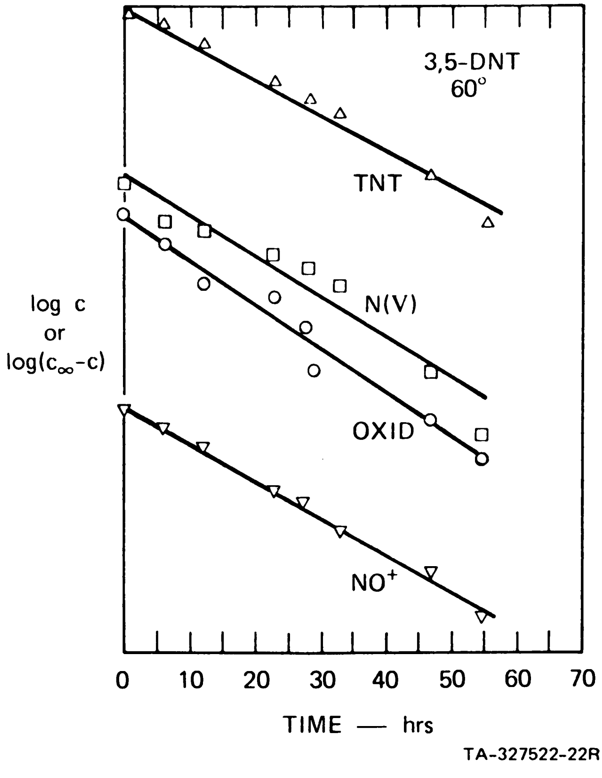


Figure 3. First-order plot of TNT production, N(V) consumption, oxidation, and NO⁺ production for 3,5-DNP at 60°

As the figure shows, there is very good agreement among the rate of consumption of N(V) and the rate of formation of TNT, the rate of DNT oxidation, and the rate of formation of N(III). The same behavior (not shown) was observed at 90°. We can conclude from the figure and the stoichiometry that the oxidation is first-order in N(V), and the first step in the oxidation is rate determining. Also, there is no autocatalytic behavior and in agreement with the earlier discussion, there is no catalysis by N(III).

The following scheme is proposed

$$\mathrm{DNT} + \mathrm{N(V)} \xrightarrow{k_n} \mathrm{TNT} + \mathrm{H}^+ \tag{7}$$

$$\mathrm{DNT} + \mathrm{N(V)} \xrightarrow[\text{(slow)}]{k_{ox}} \mathrm{DNT}_{ox} + \mathrm{N(III)} \tag{8}$$

$$\mathrm{DNT}_{ox} \xrightarrow[\text{(fast)}]{10\ \mathrm{N(V)}} 10\ \mathrm{N(III)} + \text{final organic oxidation products.} \tag{8a}$$

The results of analysis of the data in terms of this scheme are presented in Table IV. (The second-order rate constants are derived by using the mean concentrations of DNT.)

Table IV

KINETICS OF NITRATION AND OXIDATION OF 3,5-DNT AT 60° AND 90° IN SULFURIC ACID/NITRIC ACID MEDIA

	Nitration		Oxidation
Rate Constant x 10^5 (M^{-1} sec^{-1})	60°	1.10	1.64
	90°	7.52	10.05
Activation Energy (kcal/mole)	15.3		13.5

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

While it is clear from the nitration literature that in equation (7) the N(V) species participating in the nitration is nitronium ion, the active oxidant in equation (8) cannot be ascertained from these data. Thus far then, the oxidant can be nitronium ion, any species in rapid equilibrium with nitronium ion, or any combination of these species acting in parallel.

Acidity Dependence. The effect of the acidity of the medium on the rate of nitration of 2,4-DNT has been established by Bennett and coworkers, (7) and this result, along with that of other workers for the nitration of other deactivated aromatic compounds, has been recently summarized. (1) The observation is generally a steep increase in nitration rate with increasing acidity, peaking at about 90 to 95% sulfuric acid. Thereafter, with further acidity increase into oleum media, the rate declines.

The rate-increasing portion of the nitration rate profile can readily be explained by the increasing concentration of nitronium ion up to about 90% sulfuric acid, at which point the nitric acid is essentially completely converted to nitronium ion. It is not clear exactly why the nitration rate declines thereafter; however, it has been suggested that the effects of the medium on the aromatic activity coefficients are responsible. (13)

The results of our study on the acidity dependence of the rates of both nitration and oxidation of 3,5-DNT are shown in Table V. The nitration rate profile, consistent with the above discussion, shows a rate maximum in the region of 95% sulfuric acid. The oxidation rate, on the other hand, clearly displays a differently shaped profile. While the nitration rate increases by a factor of almost 200 in the interval 85 to 95% sulfuric acid, the oxidation rate in that region increases by only a factor of about 4. The oxidation rate seems to be reasonably constant above 95% sulfuric acid, whereas the nitration rate declines by a factor of about 2. Thus, there is no acid catalysis of oxidation under these conditions.

Discussion

The data for the oxidation of 3,5-DNT presented here can be summarized as follows. The rate of oxidation is (1) first order in N(V); (2) nonautocatalytic, and not catalyzed by N(III); (3) reasonably independent of medium acidity. Furthermore, the

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Table V

ACIDITY DEPENDENCE OF NITRATION AND OXIDATION RATES FOR 3,5-DNT AT 90°

Medium[a]	Acidity[b] (-H_0)	Relative Rates	
		Nitration	Oxidation
85% H_2SO_4	7.7	5.3×10^{-3}	0.26
95% H_2SO_4	8.9	1	1
15% Oleum[c]	12.3	0.58	1.2
30% Oleum[d]	12.8	0.48	1.1

[a] HNO_3:DNT = 2:1 for all runs.

[b] The Hammett acidity function. [M. Paul and F. Long, Chem. Rev., 57, 1 (1957)]. These values for pure H_2SO_4 and provide some indication of the range of acidity dealt with here. Since H_0 is a logarithmic function, each unit change in the function value corresponds to a factor of 10 change in acidity.

[c] SO_3:HNO_3 = 2:1.

[d] SO_3:HNO_3 = 4:1.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

first step involving organic substrate appears to be kinetically slow, and the ultimate inorganic product is N(III).

Nitronium ion can be ruled out as the oxidizing species in step (8) since its concentration, paralleled by the nitration rate profile, steeply climbs with increasing medium acidity. Thus, if equation (8) involved nitronium ion, the oxidation rate would display the same profile as does the nitration rate.

Molecular nitric acid can also be eliminated as the oxidizer since its concentration drops with increasing acidity. If the oxidation directly involved HNO_3, its rate would steeply decline in the stronger acidic media.

The thermal decomposition of liquid nitric acid could be important in these reactions, since it decomposes at the temperatures used here and yields potential oxidizers as products. The principal work in this area was reported by Robertson et al., (14) and Cordes et al., (15, 16) and while these authors do not agree on a detailed mechanism, there is little question that N_2O_5 is the critical intermediate in the decomposition. A reasonable mechanism for decomposition would be the sequence*

$$2\ HNO_3 \rightleftarrows H_2O + N_2O_5 \qquad (9)$$

$$N_2O_5 \rightleftarrows NO_3 + NO_2 \rightleftarrows 1/2\ O_2 + 2\ NO_2 \qquad (10)$$

The net reaction is the well known equilibrium for the production of nitric acid from nitrogen dioxide, water, and oxygen (17)

$$2\ HNO_3 \rightleftarrows 1/2\ O_2 + H_2O + 2\ NO_2 \qquad (11)$$

We suggest that the NO_2 evolved in this equilibrium is the active oxidizer in these mixed acid systems. The steps following NO_2 generation via (11) would be

$$RH + NO_2 \longrightarrow HNO_2 + R\cdot \qquad (12)$$

---

*Cordes et al. have suggested an alternative sequence involving the step (16)

$$HNO_3 \longrightarrow HO + NO_2$$

We estimate, however, that such a step would be far too slow to be consistent with the observed rates of decomposition.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

followed rapidly by (HA = strong acid)

$$HNO_2 + HA \longrightarrow NO^+ + A^- + H_2O \qquad (13)$$

The sequence (11) - (13) is consistent with all of the data presented on the oxidation. First, in this scheme the oxidation of RH is first order in N(V). Next, it is not catalyzed by N(III) due to step (13), which at these high acidities, rapidly "traps" the N(III) species in the noncatalytic NO^+ form.

Finally, that the rate of oxidation is independent of acidity can be shown through the consideration that the oxidation rate is a function of the N_2O_5 concentration. That concentration, in turn, is fixed through equilibria

$$HNO_3 + HA \rightleftharpoons NO_2^+ + H_2O + A^- \qquad (14)$$

$$NO_2^+ + A + HNO_3 \rightleftharpoons N_2O_5 + HA \qquad (15)$$

Since increased acidity drives (14) to the right, but drives (15) to the left, the net effect is that the concentration of N_2O_5 is independent of the acidity of the medium.

Thus, it appears that the thermal decomposition of nitric acid is responsible for the oxidation in these systems. The NO_2 evolved in the decomposition is the oxidizer, and the overall process is

$$HA + HNO_3 + RH \longrightarrow R + 3/2\ H_2O + NO^+ + 1/4\ O_2 + A^-$$

The evolved O_2 is undoubtedly consumed in the subsequent rapid oxidative steps (8a).

Appendix

Nitration of 2,4-, 3,4-, and 3,5-DNT

Presented below are the data for the nitration of 2,4-, 3,4-, and 3,5-DNT at 90°. The mole ratios used were $H_2SO_4:HNO_3:DNT = 10:1:0.5$. Initial DNT quantity was 8.1 ± 0.1 mmol. Product analysis was by gas chromatography. TNT yield is defined as [(total TNT)/(consumed DNT)] x 100.

DNT Isomer	Conversion[a] (%)	Products		TNT Yield[a] (%)	Product Ratios	Relative Nitration Rates
		TNT Isomer	mmoles			
2,4-	72.4	2,4,6-	5.92	93.9	--	18.1
3,4-	97.6	2,4,5-	6.31	95.7	o:o' = 4.8	29.3
		2,3,4-	1.32			
3,5-	16.0	2,3,5-	0.41	35.4	o:p = 6.8	1.0
		3,4,5-	0.06			

[a] For a 1-hr run.

On the basis of classical aromatic electrophilic substitution reasoning, (18) the presence of meta nitro substituents reduces nitration rates due to deactivation of the aromatic system toward substitution. For the present case the expected nitration rate order would then be 2,4- >3,4- >3,5-, as the molecules have 0, 1, and 2 meta nitro groups, respectively.

We were surprised to find the observed order to be 3,4- > 2,4- >> 3,5-. The rate order for the 2,4- and 3,4-isomers is in contrast to the reported results for nitrotoluene (NT), where the order is 2-NT > 3-NT. (19)

The sequence can be explained by the suggestion that the adjacent nitro substitution in the 3,4-case results in one of the nitro groups being turned from the plane of the aromatic system. Thus, only partial deactivation toward electrophilic substitution takes place, and a relatively rapid nitration is observed.

This suggestion is confirmed by inspection of Fisher, Hirschfelder, and Taylor molecular models of the isomers. For *ortho*-*di*nitro substitution such as in 3,4-DNT, only one nitro group can be aligned to be coplanar with the ring, while the other is sterically constrained out of the plane. On the other hand, in the case of nitro substitution ortho to a methyl group as in 2,4-DNT, there is no steric constraint. Thus, in 3,4-DNT, only one nitro group is fully interactive with the aromatic system, whereas for 2,4-DNT, both nitro groups participate fully.

As far as we are aware, the nitration data on 3,5-DNT are the first to be reported. The only account in the literature is an attempted nitration by Will, (2) who reported only the isolation of 3,5-dinitrobenzoic acid.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch007

Acknowledgment

We acknowledge the support of Picatinny Arsenal, Dover, New Jersey, for this work.

Literature Cited

1. Hoggett, J., Moodie, R., Penton, J., and Schofield, K., "Nitration and Aromatic Reactivity", Cambridge University Press, New York (1971).
2. Will, W., Ber. (1914) 47, 704.
3. Titov, A., Tetrahedron (1963) 19, 557.
4. Longstaff, J., and Singer, K., J. Chem. Soc. (1964) 2604, 2610.
5. Granzow, A., and Wilson, A., J. Org. Chem. (1972) 37, 1189.
6. Ogata, Y., Tezuka, H., and Kamei, T., J. Org. Chem., 34, 845 (1969).
7. Bennett, G. M., Brand, J., James, D., Saunders, T., and Williams, G., J. Chem. Soc. (1947) 474.
8. Kohlbeck, J., Chandler, C., Jr., and Dickenson, R., Final Engineering Report on Production Engineering Projects PE-238 and PE-289, Radford Army Ammunition Plant, Hercules, Inc., Radford, Va., May, 1973.
9. Holahan, J., Castorina, T., Autera, F., and Helf, S., J. Amer. Chem. Soc. (1962) 84, 756.
10. Millen, D. J., J. Chem. Soc. (1950) 2589.
11. Gillespie, R., J. Chem. Soc. (1950) 2493.
12. Frost, A., and Pearson, R., "Kinetics and Mechanism", p. 11. John Wiley and Sons, Inc., New York (1965).
13. Grabovskaya, Zh., and Vinnik, M., Russ. J. Phys. Chem. (1966) 40, 1221.
14. Robertson, G., Jr., Mason, D., and Corcoran, W., J. Phys. Chem. (1955) 59, 683.
15. Tait, W., Happe, J., Sprague, R., and Cordes, H., J. Amer. Chem. Soc. (1956) 78, 2670.
16. Cordes, H., Fetter, N., and Happe, J., J. Amer. Chem. Soc. (1958) 80.
17. Stern, A., Mullhaupt, J., and Kay, W., Chem. Rev. (1960) 60, 205.
18. Gould, E. S., "Mechanism and Structure in Organic Chemistry", p. 428 Henry Holt and Co., New York (1959).
19. Tillett, J., J. Chem. Soc. (1962) 5142.

8

Side Reactions During Aromatic Nitration

C. HANSON, T. KAGHAZCHI* and M. W. T. PRATT

Schools of Chemical Engineering, University of Bradford, Bradford England, and
*Institute of Chemical and Petrochemical Engineering,
Tehran Polytechnic, Tehran, Iran

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Aromatic nitration has long been an important process in industrial chemistry for nitro-aromatic products are widely used as explosives, solvents, pharmaceuticals and intermediates in the manufacture of synthetic dyestuffs and other chemicals. The nitrating agent most commonly used industrially for aromatic mononitrations is an aqueous mixture of nitric and sulphuric acids, typically 15 mole % HNO_3, 30 mole % H_2SO_4 and 55 mole % H_2O. The organic substrate, together with the nitro product, forms a separate phase from the aqueous mixed acid and so mass transfer is involved simultaneously with chemical reaction. The reaction mixture should be well stirred, therefore, to minimise the mass transfer resistances, although these may never be completely overcome. The mixed acid generally gives the wanted nitro product more quickly, at a lower temperature and with less loss through higher oxidation reactions than when nitric acid alone is used.

Aromatic nitration also has been of great importance in the development of the theory of organic chemistry and has received much attention as an example of electrophilic substitution. As a result of this, the involvement of the nitronium ion, NO_2^+, as the nitrating agent adding to the aromatic ring has been well established, although the great majority of theoretical studies of the kinetics and mechanism have been carried out with systems which are homogeneous and either anhydrous or contain a relatively low concentration of water. This is in contrast with the two-phase aqueous systems used so widely in commercial aromatic nitration. The effect on the reaction of water, which is known to decrease nitronium ion concentration, is discussed in another paper contributed to this symposium by some of the present authors, but the generally accepted view at present is that the nitronium ion mechanism still applies to aromatic nitration in the mixed acid system. It is quite clear, however, that side reactions do occur, even during mononitration reactions. In the mononitration of toluene, for example, the pure nitro products, toluene and spent nitrating acid, are pale

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

in colour and yet the organic and aqueous phases of the reaction mixture are sometimes highly coloured, from strong yellow to dark red. Product yields are usually less than 98% and the occurrence of phenolic and other impurities has been reported in the literature.

Side reactions are important for several reasons:-

Economic considerations. By-product formation represents loss of reactants or nitro product. It is also likely to result in increased costs for the separation and purification of the main product, such as increased capital costs for distillation and washing stages, together with higher operating costs for steam and treatment chemicals.

Environmental considerations. By-products often appear as pollutants discharged from the manufacturing plant as constituents of gaseous, liquid or solid effluents. The pollution of the environment by chemical effluents is of increasing concern and further legal constraints and limits are likely to be imposed. Phenolic impurities, commonly found as by-products of aromatic nitration, are particularly harmful in the damage they cause in water courses because of their high toxicity.

Safety factors. By-product formation may involve a safety hazard: for example, the presence of even small quantities of chemically unstable impurities, such as highly nitrated compounds, may catalyse explosive decompositions.

For all these reasons, avoidance or reduction of by-product formation would be of clear benefit, but as previous knowledge of side reactions during aromatic nitration reported in the literature is not comprehensive, this further investigation has been made. The aims were to characterise the by-products formed during the mononitration of toluene and some other aromatic compounds, and to measure the rate and extent of production of by-products as a function of reaction conditions so that the effect of side reactions may be minimised. Particular attention has been given to the formation of nitrous acid and organic acid by-products as these appear to be the major impurities during toluene mononitration.

At present, it is normal practice to remove the phenolic by-products from aromatic nitro products by washing the product successively with water and aqueous caustic soda. The alkaline washings are commonly acidified to free the bulk of the phenols, which may be separated for disposal, for example, by burning. A proportion of them, however, remains dissolved in the aqueous effluent. An alternative process is suggested here for removal of the acidic organic by-products which avoids continuous consumption of caustic soda and acid. This could have economic advantages through lower operating costs as well as a reduction in the phenol concentration of the plant effluent.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Literature Survey

During the last ninety years, studies of aromatic nitrations reported in the literature have revealed that small quantities of hydroxy by-products are generated in these reactions, their nature and quantity being dependent chiefly upon the particular type of aromatic compound and the nitrating system. Noelting and Forel(1) in 1885 reported that, in the mononitration of toluene, nitrocresols are formed and if they are not removed by an alkali wash, they undergo further nitration to trinitrocresol or oxidation to oxalic acid. In 1889, Noelting and Pick(2) isolated dinitro-o-xylenol in the preparation of nitro-xylene and in 1891 Armstrong and Rossiter(3) noticed that phenolic compounds were formed during the nitration of benzene and toluene. Following these initial reports, similar phenolic by-products were found during many aromatic nitrations. In 1933, Berkenheim and Coster(4) suggested that the mechanism of formation of hydroxy by-products could involve a rearrangement of complex nitrite ethers. Titov and Baryshnikova(5) found in 1936 that, in the nitration of toluene by dinitrogen dioxide in the presence of sulphuric and phosphoric acids, about 2% of 2,6 dinitro-p-cresol is produced. They first suggested a mechanism involving reaction of nitrous acid with toluene to give a diazonium hydroxide, which loses nitrogen to yield a phenol. Later, Titov(6) proposed a different reaction scheme in which NO^+ reacts with the aromatic to form a nitroso compound which rearranges to a nitrophenol. This mechanism will be discussed later. Bennett and Youle(7,8,9) also found phenolic impurities amounting to about 2% of the yield in the nitration of several different aromatic compounds. They observed that the hydroxyl group enters the aromatic molecule according to the normal orientation rule for the substituent originally present and that the amount of by-products is greater for meta-directing substituents.

The most comprehensive contribution to knowledge of side reactions during aromatic nitration up to the present time has been made by Dadak and co-workers in a series of four papers(10-13). During toluene nitration, they detected the formation of nitrocresols, p-nitrophenol, 4,6 dinitrocresol, 2,4 dinitrophenol and 3 nitro-4 hydroxy-benzoic acid. They reported some quantitative analyses for this and other nitrations, although they did not investigate a wide range of reaction conditions. They suggested that the by-products originated from the oxidation of toluene to cresols, followed by mono-, di- or tri-nitration, the presumed reaction schemes being shown in Fig.1, in which the compounds shown in square brackets were not isolated. No explanation for the mechanism of introduction of the hydroxyl group was given and no attention was given to nitrous acid formation.

The gaps and inconsistencies in previous investigations

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

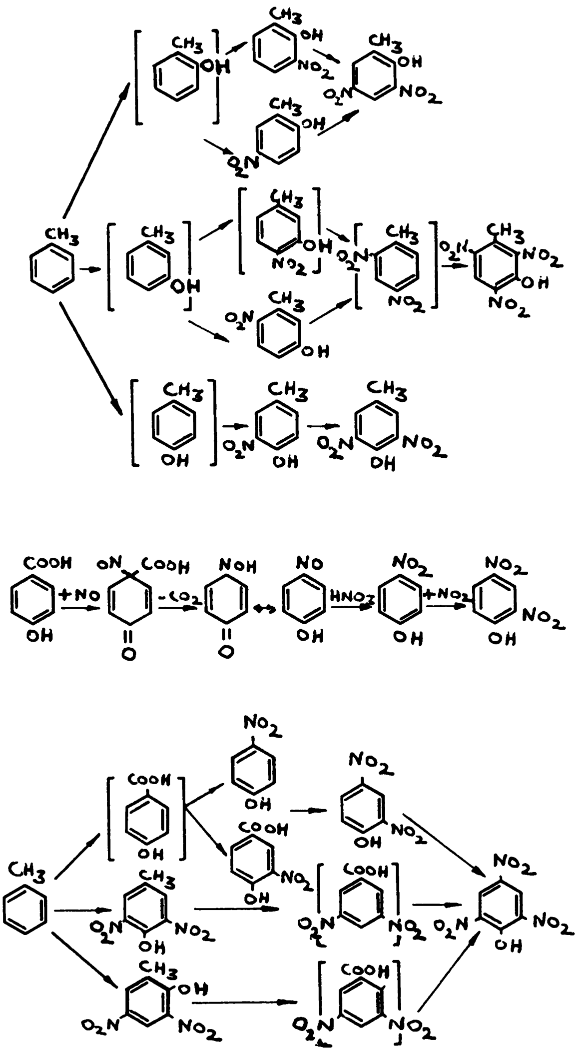


Figure 1. Reaction schemes suggested by Dadak et al.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

reported in the literature, a more complete account of which is given elsewhere(14), clearly leave room for further work on side reactions during aromatic nitration.

Experimental Results and Discussion

The experimental programme was divided into the following aspects, which are reported separately:-

(1) formation of nitrous acid during the heterogeneous nitration of toluene.

(2) formation of organic acid by-products and their quantitative relation with nitrous acid.

(3) effect of sulphuric acid concentration upon organic acid by-product formation.

(4) by-product formation from other substrates.

(5) effect of addition of urea and nitrite ion on by-product formation.

Further experimental work concerned with the development of an alternative process for the removal of phenolic by-products from nitro products is discussed in a final section.

Formation of Nitrous Acid during the Heterogeous Nitration of Toluene. Known volumes of the aromatic hydrocarbon were mechanically shaken at a constant speed with twice the volume of nitrating acid (30 mole % sulphuric acid, 15 mole % nitric acid, 55 mole % water) in a stoppered flask immersed in a thermostat at 25.0° ± 0.1°C. After a period of time, the contents of the flask were poured into a separating funnel and the unwashed organic and aqueous phases analysed for nitrous acid by a colorimetric method using sulphanilic acid and α-naphthylamine. The aqueous and washed organic phases were then analysed for mono-nitrotoluene (MNT) by UV spectrophotometry using the absorption peak at 350 nm. The nitrous acid content of the fresh mixed acid used was less than 10^{-4} moles/l.

As Fig.2 shows, the nitrous acid concentration (total moles nitrous acid divided by total volume of both phases) increases with time, approximately in proportion to the concentration of MNT formed. The rate of formation decreases towards the end of the reaction between toluene and nitric acid. The distribution coefficient for nitrous acid between the two phases, $[HNO_2]$org./$[HNO_2]$aq., decreases from 0.48 towards the start of reaction to 0.28 near the end.

To determine whether nitrous acid is formed only from the toluene present, the experiment was repeated with MNT instead of toluene as the aromatic compound present initially. Nitrous acid was produced at approximately the same rate as from toluene (Fig.3). This indicates that the decrease in rate of nitrous acid formation towards the end of the main reaction is because the nitric acid has been nearly used up, rather than being due to the replacement of toluene by MNT.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

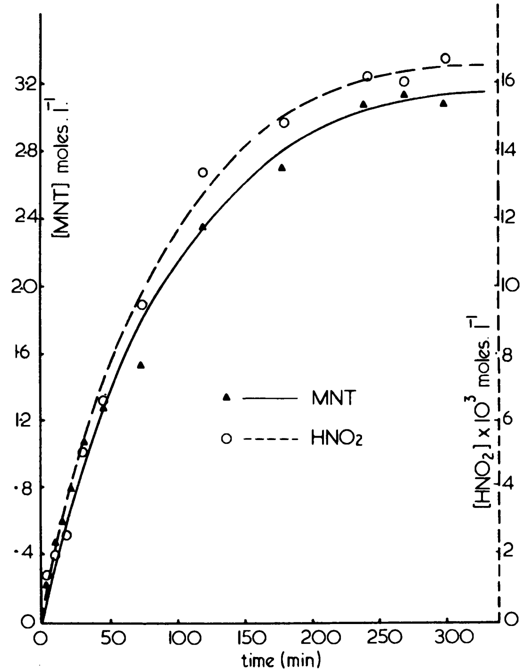


Figure 2. Production of MNT & HNO_2 during the nitration of toluene with mixed acid

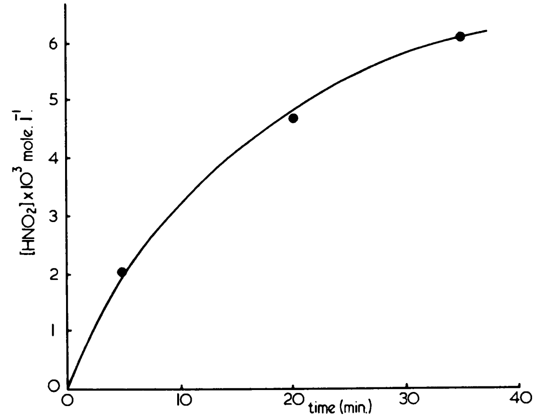


Figure 3. Production of HNO_2 during the reaction of MNT with mixed acid

The effect of change in reaction conditions upon the rate of formation of nitrous acid was measured in a series of experiments A to F. The results are shown in Fig.4. In experiment A, industrial mixed acid is used at 25°C with an organic/aqueous phase ratio of 0.5. In B, the concentration of nitric acid is reduced from 15 to 3 mole %. The concentration of sulphuric acid is lower in C:20 mole % instead of the normal 30%, the nitric acid being the usual 15 mole %. The temperature is increased to 35°C in D, with normal mixed acid, and in E the phase ratio is increased to 1.0. Finally, in F, nitric acid (70%) is used alone, without sulphuric acid.

On the basis of these experiments, the rate of formation of nitrous acid is seen to be very dependent upon sulphuric acid concentration. Nitrous acid production decreases with increase in sulphuric acid concentration in the mixed acid, although MNT production is enhanced by increase in sulphuric acid content. In C, for example, the nitrous acid represents 2 mole % of the MNT.

The plot of the concentration of MNT versus nitrous acid is a straight line for each experiment (Fig.5) which indicates that nitrous acid and MNT are produced in constant proportion. The ratios [HNO_2]/[MNT], although constant during each experiment, vary with reaction conditions as follows:

(1) the ratio increases with increase in nitric acid concentration (at constant sulphuric acid concentration)

(2) it decreases with increase in sulphuric acid concentration (at constant nitric acid)

(3) the ratio increases with increase in reaction temperature

(4) it increases with increase in volume ratio of organic to aqueous phase from 1:2 to 1:1

(5) in the absence of sulphuric acid, large quantities of nitrous acid are formed and the ratio [HNO_2]/[MNT] is particularly high.

To establish whether nitrous acid is produced mainly from attack on toluene or nitrotoluene, about 20 ml of the aromatic compound was shaken with an equal volume of dilute (6N) nitric acid in a stoppered flask at 25°C for 16 hours, after which the nitrous acid formed was measured. Nitric acid of this concentration is not strong enough to nitrate toluene under these conditions, no trace of MNT being detectable by UV analysis of the organic layer after 24 hours. The initial concentration of nitrous acid in the 6N nitric acid used was 1.5×10^{-5} moles/l. This increased when shaken with the aromatic compound to 8.15×10^{-5} moles/l in the case of toluene and to 2.85×10^{-4} moles/l for MNT. These results do not represent the total nitrous acid formed during the reaction, as some of it would decompose during the 16 hour period. They do confirm, however, that nitrous acid may be formed from both toluene and MNT even by the action of dilute nitric acid. The kinetics of reaction between dilute nitric acid, up to 8N strength, and MNT to produce nitrous acid were followed over a two week time interval in homogeneous acetic acid solution. With both excess

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

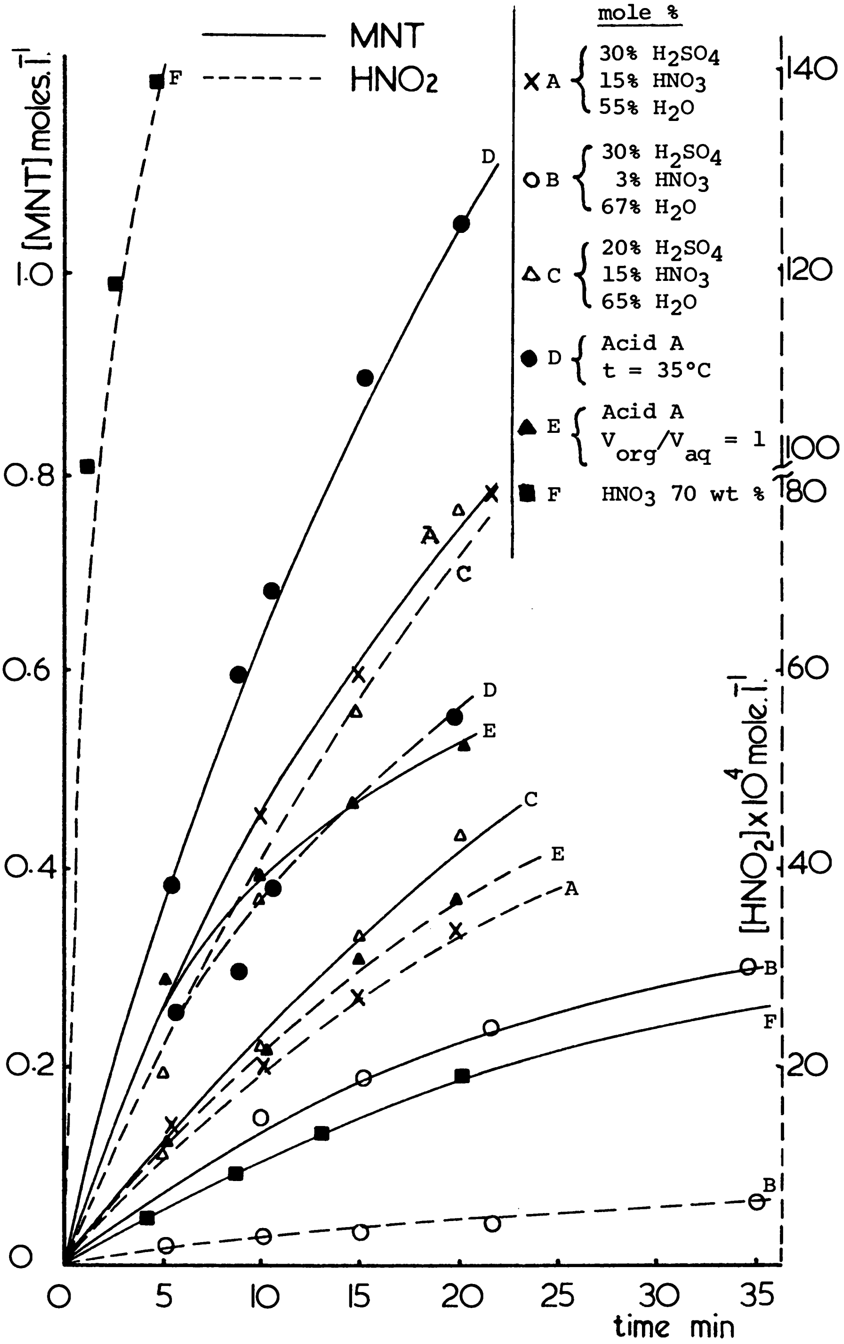


Figure 4. Production of MNT & HNO_2 under various reaction conditions

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

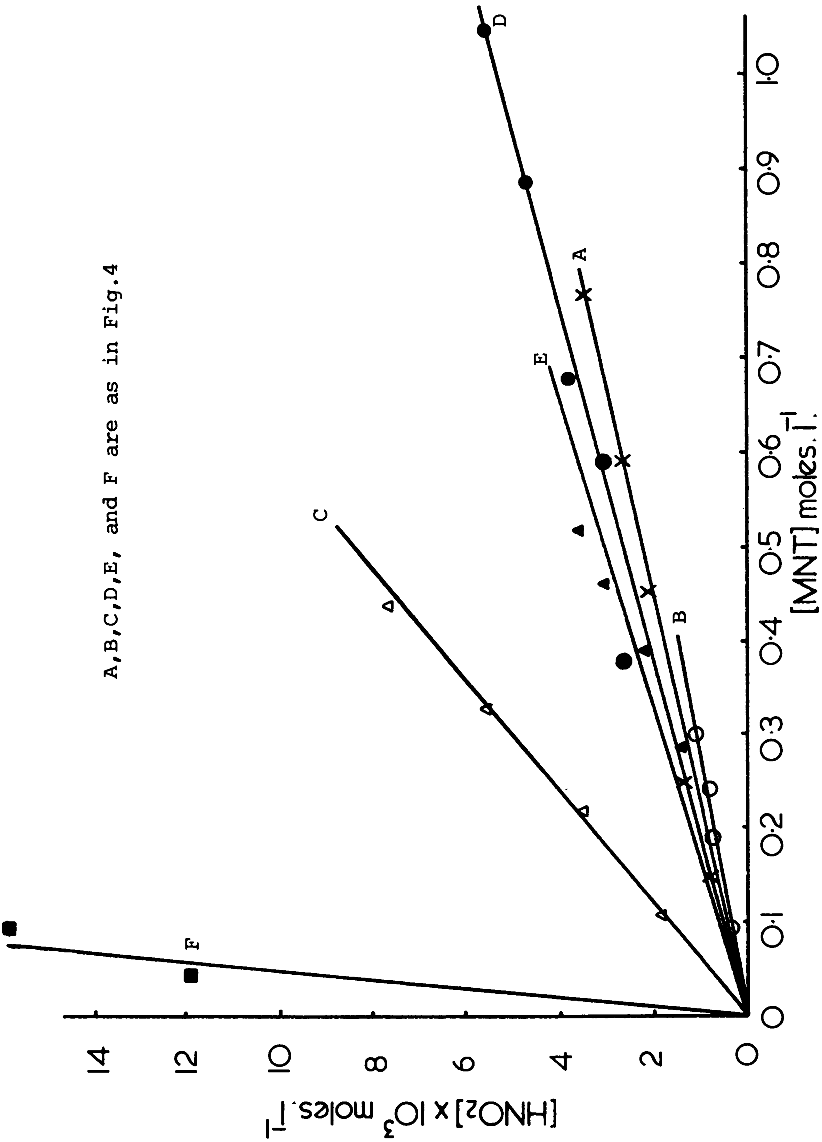


Figure 5. *The effect of reaction conditions on the ratio* $[HNO_2]/[MNT]$

MNT and excess nitric acid, the concentration of nitrous acid reaches a maximum and then falls as the rate of nitrous acid decomposition exceeds its formation rate. Detailed results of this work are given elsewhere(14).

Formation of Organic Acid By-products and their Quantitative Relation with Nitrous Acid. If the raw MNT product containing by-products is dissolved in a solvent such as carbon tetrachloride or chloroform and subjected to infra-red analysis, the absorption peaks correspond to MNT and dissolved nitric acid; peaks due to organic by-products are not generally seen, as they are below the detection limit under these conditions. The presence of phenolic compounds may be confirmed if they are concentrated by extraction into aqueous alkali, which is then acidified to liberate free acids for re-extraction by a small quantity of organic solvent. Another confirmatory test involves the KBr pressed disc technique, in which a thin film of the organic phase product is examined. The large excess of MNT compared with the by-products makes this method unsuitable for quantitative analysis. It did indicate, however, that neutral or basic organic impurities were not present in large amounts as no significant absorption peaks which could correspond to such compounds were found, although peaks corresponding to phenols were identified.

The general technique used for extraction of by-products was, therefore, that of alkali extraction. The organic product phase was washed three times with 2N sodium hydroxide to extract the water-soluble salts of the organic acids. Hydrochloric acid was added to liberate the organic compounds for extraction by ether. Following evaporation of the ether, the residual by-products were weighed. In some cases traces of common salt, which is slightly soluble in ether, contaminated the organic by-products; a recrystallisation from chloroform was then performed.

A portion of the organic by-products was dissolved in carbon tetrachloride or chloroform (spectroscopic grade) for infra-red analysis. The absorption peaks corresponded to nitrophenols, nitrocresols, dinitrophenols, dinitrocresols, traces of trinitro compounds and nitro-hydroxy carboxylic acids. The presence of individual compounds was confirmed by comparison with the absorption spectrum of the pure compounds and by thin-layer chromotography. Quantitative analyses of the concentrations of several components of the by-products were made. If a component did not have an absorption band free from interference by another constituent of the mixture, quantitative analysis could still be achieved by measurement of the extinction coefficients of the interfering components at several different frequencies, together with the absorbance of the mixture at these frequencies. Characteristic absorption bands used are shown in Table I.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

TABLE I

Characteristic IR Absorption Bands

Compound	Wavenumber(cm^{-1})
2, 6 dinitro p-cresol	875
4, 6 dinitro o-cresol	950 and 1090
2, 4 dinitrophenol	1140 and 1110
p-nitrophenol	1110 and 860
mono-nitrocresols	860
3 nitro 4 hydroxy benzoic acid	1730

The results of quantitative analysis of the by-products from nitration of toluene by standard mixed acid are given in Table II. The major constituent is 2, 6 dinitro-p-cresol, representing almost 80% of the acidic organic by-products. The six components listed represent 99% of the total and therefore represent all major constituents of the mixture, for which the weighted mean molecular weight is 198.

TABLE II

Composition of Organic Acid By-Products

Compound	% by weight
2, 6 dinitro p-cresol	79.6
4, 6 dinitro o-cresol	10.3
2, 4 dinitrophenol	1.4
p-nitrophenol and mono-nitrocresol	4.3
3 nitro 4 hydroxy benzoic acid	3.3
TOTAL	98.9
Mean Molecular Weight	198

An interesting relation between the amounts of nitrous acid and organic acid by-products became apparent. The concentrations of the organic by-products formed from the nitration of toluene under various reaction conditions are plotted in Fig.6 against the concentrations of nitrous acid produced in the same experiment. The relationship is approximately linear, showing that nitrous acid and organic acids are formed in a constant proportion. From the best straight line, it is seen that 6×10^{-2} moles/l of nitrous acid are produced for 12 g/l of organic by-products. From the mean molecular weight of the mixture of by-products, 12 g/l is equivalent to 6.0×10^{-2} moles/l. Within experimental error, one mole of organic by-product is formed for each mole of nitrous acid. The mechanisms of formation of these two by-products are therefore likely to be directly linked.

During these experiments, a constant high degree of agitation was used so that reaction times were all relatively

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

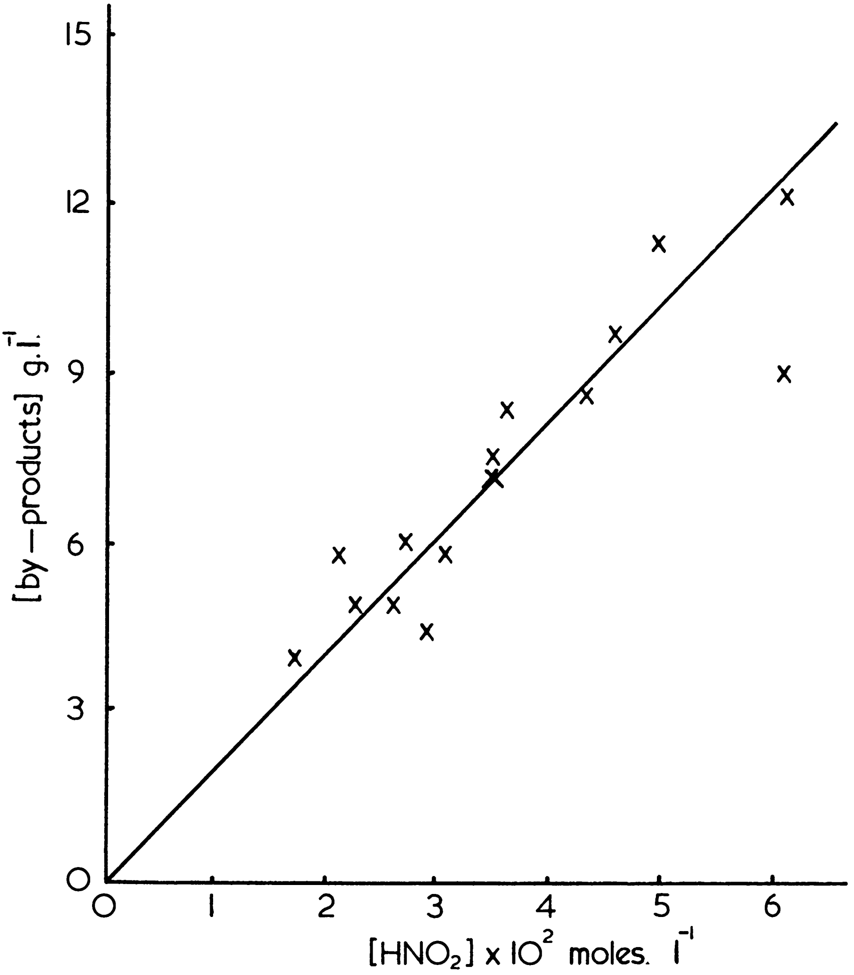


Figure 6. The relationship between HNO_2 and organic by-products formed

short and any decomposition of nitrous acid would be minimal.

For comparison, the formation of nitrous acid and organic by-products during nitration under homogeneous conditions was determined, acetic acid being used as solvent. The reaction mixture contained 0.3 moles/l toluene and 10.06 moles/l nitric acid with varying concentrations of sulphuric acid. Reaction temperature was 25°C. Again, a one to one molar ratio was found between nitrous acid and organic acid by-products over a time up to one hour during which about 98% conversion of toluene to MNT was obtained. As further time elapsed, the concentration of organic by-products decreased but nitrous acid continued to increase. This could be because an excess of nitric acid was used which, after completion of mononitration of toluene, could react further with the organic by-products causing their degeneration and producing further nitrous acid. Increase in sulphuric acid concentration, as for heterogeneous reaction, increased the rate of production of MNT and decreased the proportion of by-products to MNT.

Effect of Sulphuric Acid Concentration upon Organic Acid By-Product Formation. It is known that increase in sulphuric acid concentration increases the rate of aromatic nitration but its effect on by-product formation had to be found. Three series of experiments were made at 35°C, in each of which nitric acid concentration was kept constant at 15 mole %, while sulphuric acid concentrations were respectively 25, 30 and 35 mole %. The organic/aqueous phase ratio was 2/3 in all cases. Plots of the variation with time of organic acid by-product concentration are given in Fig.7, and of MNT concentration in Fig.8. Clearly, increase in the sulphuric acid proportion in mixed nitrating acid increases the rate of formation of MNT, as expected, but it decreases the formation of organic by-products.

This result is of significance for the operation of commercial plants for aromatic nitration. It indicates that higher yields of MNT may be achieved if the proportion of sulphuric acid is increased towards the limit of about 37 mole % sulphuric acid, 15 mole % nitric acid and 48 mole % water, at which the onset of dinitration is just detected. Increase in sulphuric acid concentration from the normal 30 mole % to 35 mole % decreases organic by-product formation by over 25%.

By-Product Formation from other Substrates. The formation of nitrous acid and organic acid by-products during the heterogeneous nitration of other substrates was compared with the corresponding results during toluene mononitration. Besides toluene, the hydrocarbons studied were benzene, ethylbenzene, o-, m- and p-xylenes and mesitylene. In all cases, the normal mixed nitrating acid composition was used with organic/aqueous phase ratio of 2/3 and reaction temperature of 35°C. Fig.9 shows that the rate of formation of the mononitro products does not follow

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

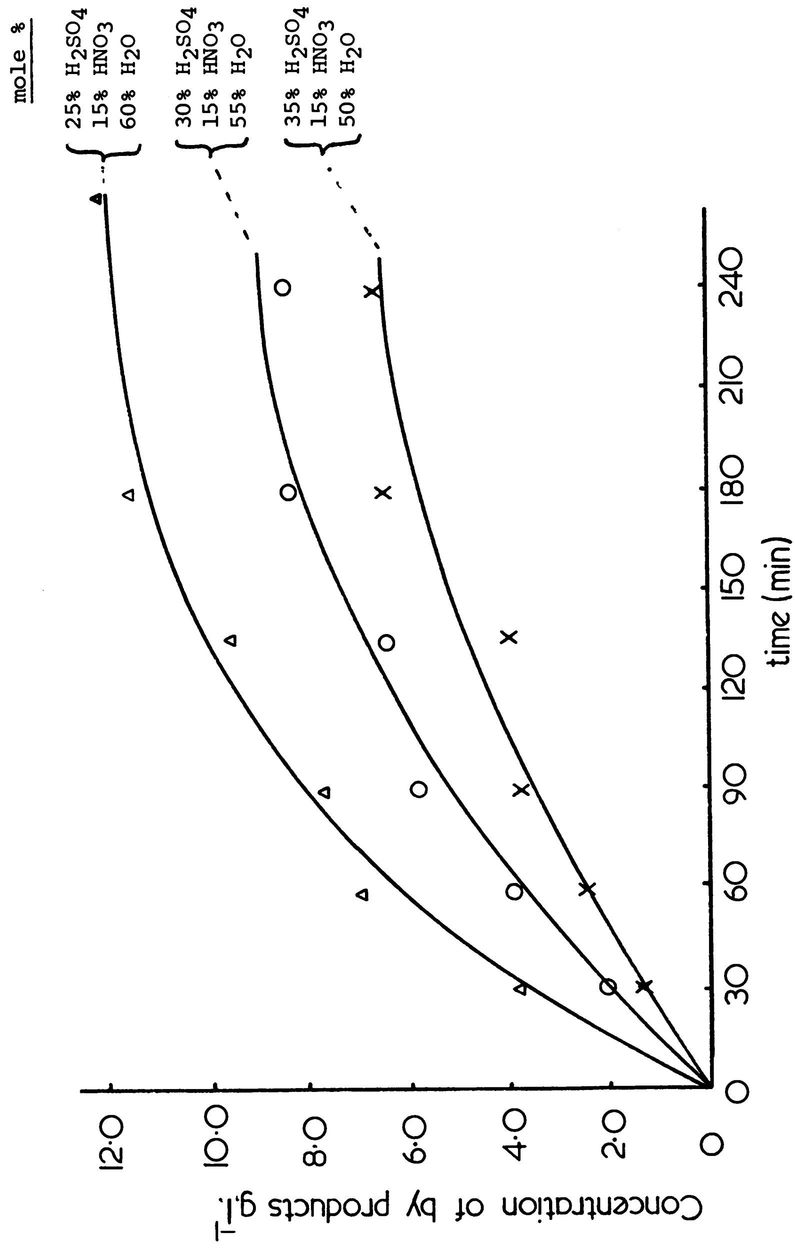


Figure 7. The effect of H_2SO_4 concentration on the rate of production of by-products

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

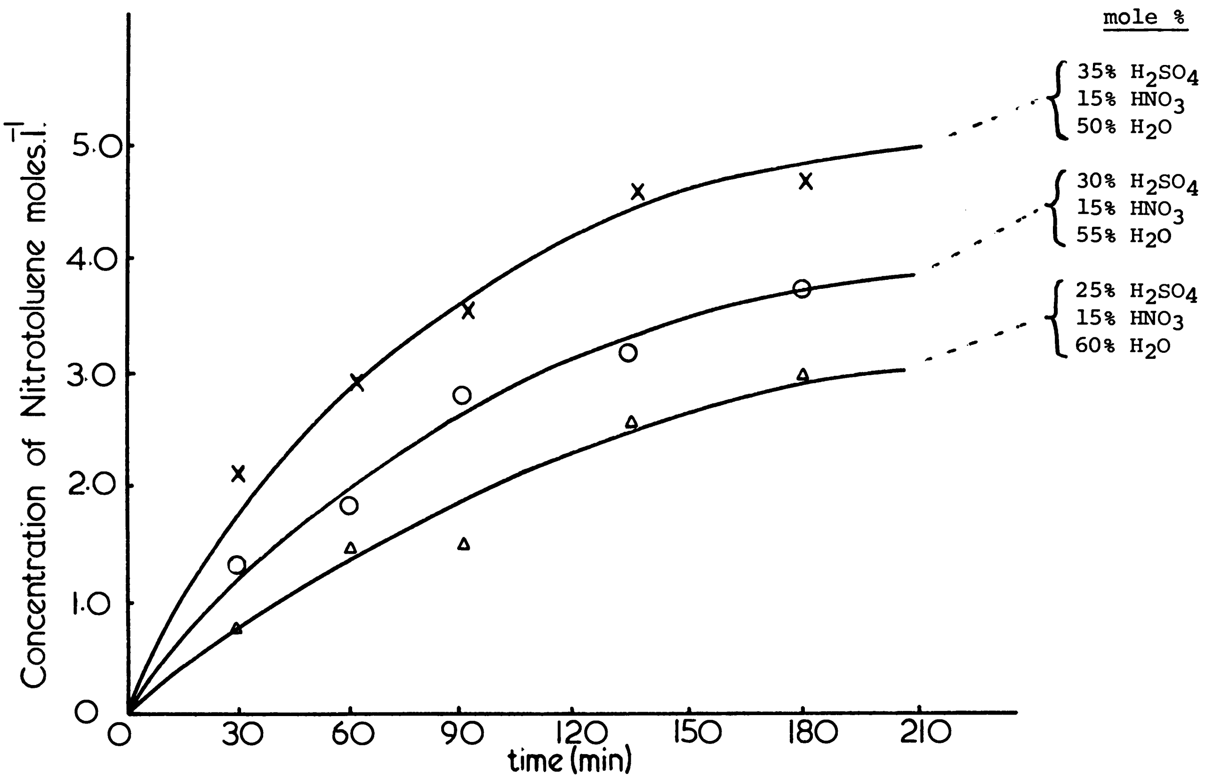


Figure 8. The effect of H_2SO_4 concentration on the rate of production of nitrotoluene

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

the ordinary rule of reactivity of aromatic hydrocarbons in homogeneous solution (benzene < ethylbenzene ≤ toluene < o-, m- and p-xylene < mesitylene) for the rates of nitration of m- xylene and mesitylene are below that of toluene in this two-phase nitration, as has been noted before(15). The corresponding production of organic acid by-products is given in Fig.10, which shows that, of the aromatic hydrocarbons investigated, o- and p-xylene are most prone towards by-product formation. Benzene forms negligible quantities of by-products; m-xylene and mesitylene, which have high reactivity towards nitration, are next lowest, below toluene and ethylbenzene. For all the aromatics, the ratio of organic acid by-products to nitro-aromatic product is almost constant with respect to time. The average yield of organic acidic by-products compared with the nitro aromatics is listed in Table III.

TABLE III

Organic By-Product Yield from Various Hydrocarbons

Hydrocarbon	Weight % organic by-products compared with mononitro compound
benzene	0.018
toluene	1.72
ethylbenzene	1.63
o-xylene	6.19
p-xylene	3.13
m-xylene	0.77
mesitylene	1.31

Formation of nitrous acid during the nitrations (Fig.11) shows the same relative variation as that of the organic by-products.

Effect of Addition of Urea and Nitrite Ion on By-Product Formation. The effect of addition of 0.1 mole/l of urea and, separately, 0.1 mole/l of sodium nitrite on toluene nitration was examined but, within experimental error, no difference was detected in the quantities of organic acid by-products formed. The implications of these observations in deciding the likely mechanism of by-product formation are discussed in the next section.

Mechanism of By-Product Formation

The extensive work of Dadak and co-workers(10-13), in the course of which many by-products of aromatic nitration were identified, did not include any well-established explanation of the mechanism by which phenolic intermediates are produced and

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

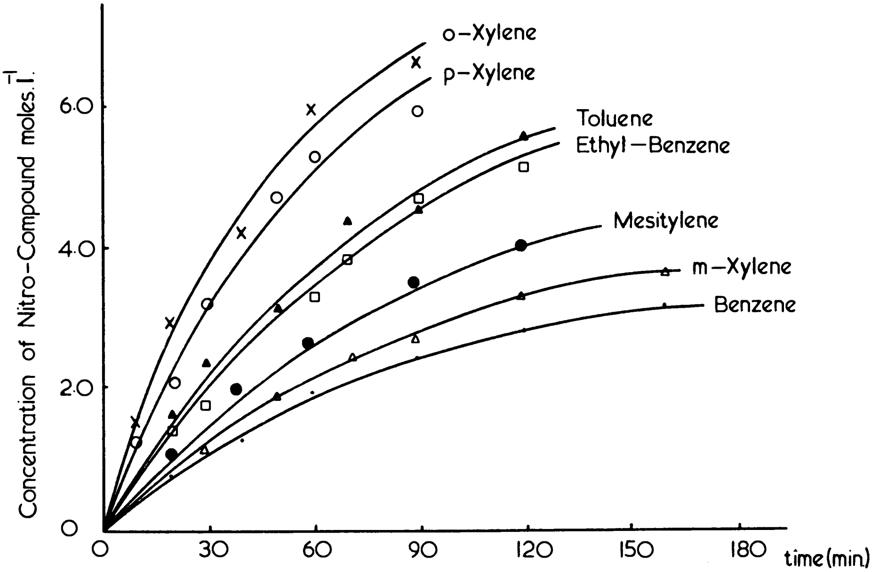


Figure 9. Nitration of various aromatic hydrocarbons by mixed acid at 35°C

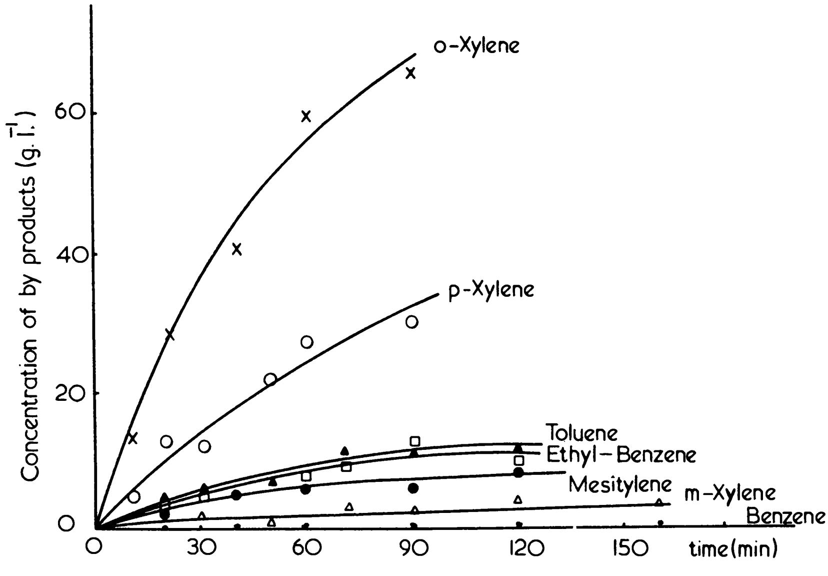
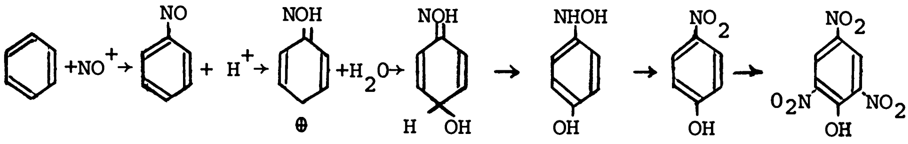


Figure 10. Formation of by-products during the nitration of various aromatic compounds

did not discuss the involvement of nitrous acid. Two reaction mechanisms are prominent among those which have been suggested previously. One of the schemes put forward by Titov(6) postulates reaction between the aromatic compound and the nitrosonium ion, NO^+. A nitroso compound is first formed which undergoes rearrangement to a phenol and may be nitrated to a mono-, di- or tri-nitrophenol:-



If this mechanism were accepted, then addition of urea, which removes any nitrous acid or NO^+ present in the nitrating mixture, should prevent or reduce the formation of by-products. On the other hand, the addition of nitrite ion should promote by-product formation:-

$$HNO_2 + H^+ \rightarrow H_2NO_2^+ \rightarrow H_2O + NO^+$$

It was noted that addition of urea or sodium nitrate has no effect on the formation of organic by-products during toluene nitration. This evidence implies that this mechanism does not play a significant part in by-product formation.

A second mechanism, for which urea or nitrite ion would be predicted to have no effect on phenolic by-product formation, has been suggested by Bennett(16,17) and also Titov(18). This supposes that a nitronium ion becomes attached to the aromatic ring through one of its oxygen atoms instead of the normal nitrogen atom, to form an aryl nitrite. This then decomposes to a phenol and a nitrosyl ion:-

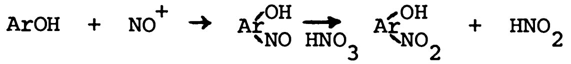
$$Ar{-}H + O = \overset{+}{N} = O \rightarrow ArO{-}N = O + H^+$$

$$ArO{-}N = O + H^+ \rightarrow ArOH + NO^+$$

A mononitro-phenol or cresol may then nitrate further to dinitro or higher compounds. The NO^+ ion ultimately becomes nitrous acid (in the absence of urea) either by:-

$$NO^+ + NO_3^- \rightarrow N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$

or



$$ArOH + NO^+ \rightarrow Ar\begin{smallmatrix}OH\\NO\end{smallmatrix} \xrightarrow[HNO_3]{} Ar\begin{smallmatrix}OH\\NO_2\end{smallmatrix} + HNO_2$$

This is in accord with the observation that 1 mole of nitrous acid is formed for each mole of organic acid by-products.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

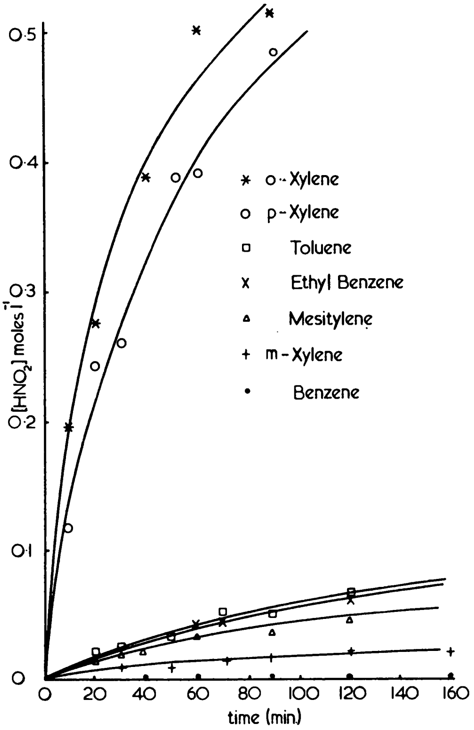


Figure 11. Production of nitrous acid during the nitration of various aromatic compounds

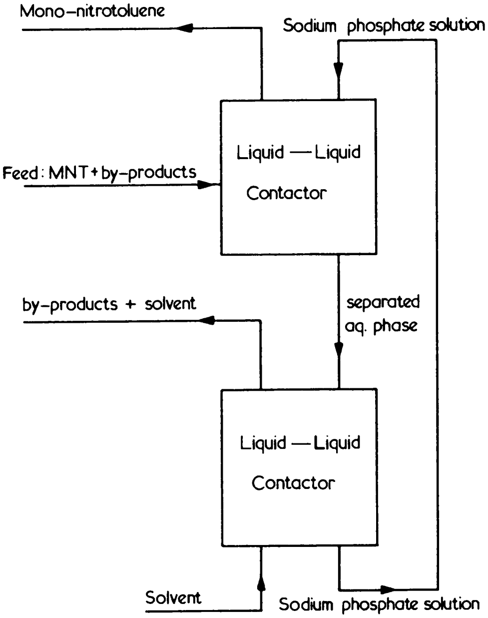
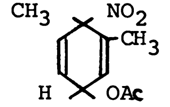


Figure 12. Flow-sheet for extraction of phenols by dissociation extraction

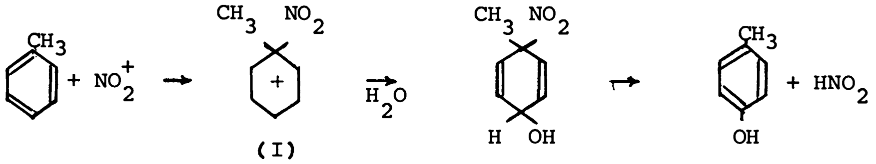
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

However, there is no confirmatory evidence that the nitronium ion may react with an aromatic ring in this manner.

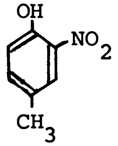
An alternative and more likely explanation, for which we are grateful to Dr. R.G. Coombes(19) who first drew it to our attention, is that an addition-elimination type of mechanism applies, similar to that proposed by Blackstock et al(20) in the autoxylation of o-xylene by nitric acid in acetic anhydride. In this reaction, intermediates positively identified were the cis and trans isomers of:-



which decompose to 4-acetoxy-o-xylene. Many similar adducts are now known. This type of ipso-nitration mechanism could be responsible for phenolic by-products during aromatic nitration; reaction by nitronium ion at the aromatic carbon to which the methyl group is attached being followed by attack by water and then by the elimination of nitrous acid:



Under homogeneous conditions, this is believed to occur(21): at high acidity, (I) rearranges giving o-nitro toluene and at low acidities the p-cresol is detected as:-



Removal of Phenolic By-Products

To free the aromatic nitro products from the phenolic impurities, two alternative procedures may be compared with the extraction process commonly used industrially at present. In this, the organic product layer after nitration is first washed with water to remove free acids and then washed with dilute sodium hydroxide (usually 1 to 4N, 15% excess). The separated aqueous phase is neutralised by excess mineral acid to liberate the phenols, 60% to 80% of which separate and may be removed. The aqueous phase is still saturated with phenols and is an obnoxious effluent. The process also involves the continuous consumption of caustic soda and strong acid, with consequent high operating costs.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

As a first alternative, the aqueous wash liquor, after acidification as before, may be treated with an organic solvent immiscible with water. This dissolves the phenols and, after separation, the solvent may be distilled and recycled. This type of extraction process for phenols is well known but to illustrate its possibilities, Table IV lists measurements of the ability of 50 ml samples of various organic solvents to remove phenolic compounds from 100 ml of the aqueous phase obtained by alkaline extraction of MNT product, followed by acidification in the usual way. The aqueous phase contained 0.4 g of phenols.

The solvent with the highest affinity for the phenols is MIBK, which removes 98% of the impurities. Two contact stages with such a solvent should reduce the phenol content of the aqueous phase to an acceptable level. However, this process would still involve the continuous consumption of strong base and acid plus some loss of MIBK by solution.

TABLE IV

Efficiency of Organic Solvents in Removing Phenolic Nitration By-Products

Solvent	Wt. of Phenols (g) extracted (total present:- 0.4 g)	% Extraction
diethyl ether	0.369	92
chloroform	0.281	70
methyl isobutyl ketone (MIBK)	0.393	98
cyclohexane	0.229	57
carbon tetrachloride	0.319	79
dichloroethane	0.311	78
benzene	0.353	88
toluene	0.328	82

A more novel process was considered, based upon the process of dissociation extraction using weakly acidic or basic reagents which has been developed by some of the present authors(22,23). For the extraction of phenolic by-products, the method is based upon contact between the organic phase containing the acidic phenols and an aqueous phase containing a weakly basic reagent, such as a phosphate salt. There should be sufficient affinity for reaction to result in essentially all the phenols being extracted into the aqueous phase as their dissociated salts, i.e. the equilibria in reactions (1) and (2) should be towards the right hand side:-

$$\mathrm{ArOH} + \mathrm{PO_4^{3-}} \rightleftarrows \mathrm{ArO^-} + \mathrm{HPO_4^{2-}} \qquad (1)$$

or

$$\mathrm{ArOH} + \mathrm{HPO_4^{2-}} \rightleftarrows \mathrm{ArO^-} + \mathrm{H_2PO_4^-} \qquad (2)$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

The aqueous phase, after separation from the purified organic product, is then contacted with an organic solvent having a high affinity for undissociated phenols. The extraction reactions (1) and (2) are then reversed in the aqueous phase, regenerating the original phosphate salt extractant, which may be recycled, while the liberated phenols are extracted into the organic phase. After separation, the organic solvent phase is distilled to recover the phenols and purified organic solvent for recycle. The separation is achieved, therefore, without the continuous consumption of chemicals and the operating costs should be reduced. Several counter-current contact stages will be necessary to achieve both an efficient extraction of the phenols from the nitro product and also their recovery from the aqueous extract phase into the organic solvent. The principles of the flow sheet are illustrated in Fig.12.

The phenolic by-products of toluene nitration have pK_a values at 25°C in the range 4 to 8, which may be compared with the three pK_a values for o-phosphoric acid of 2.12, 7.20 and 12.30. If trisodium phosphate is used as the separating reagent, the extraction of phenols is essentially complete but the equilibrium of reaction (1) lies far over to the right hand side, the phenols being much stronger acids than HPO_4^{2-}. The reaction is therefore difficult to reverse on contact with an organic solvent. A more balanced reaction is obtained with disodium hydrogen phosphate. However, $H_2PO_4^-$ is a stronger acid (pK_a = 7.20) than some of the more weakly acid phenols, which will not be extracted by this reagent. In fact, the percentage extraction of phenols when this salt was used alone was never greater than 65%. Therefore, a mixture of the two phosphate salts was used containing the minimum proportion of sodium o-phosphate. A suitable mixture, giving virtually complete extraction of the phenolic by-products, was an aqueous solution containing 64.2 g/l of $Na_2HPO_4.2H_2O$ with 21.9 g/l of $Na_3PO_4.12H_2O$. Benzene and MIBK were found to be efficient solvents for the back extraction of the phenols. Distribution of the phenols, present in varying amounts, between this aqueous phosphate solution and benzene or MIBK is shown in Table V and the number of stages required for a counter-current back extraction of phenols may be obtained by a McCabe-Thiele type calculation. It is not necessary, of course, to recover 100% of the phenols from the aqueous phosphate stream before it may be recycled.

Initial economic comparison of the dissociation-extraction type process with the chemical-consuming process of caustic wash, acidification, and solvent extraction indicates that the dissociation extraction process, which has lower operating costs but may have higher capital cost for contactors and associated equipment, may be less costly overall. A process optimisation and more detailed economic assessment would have to be made, however, before a definite decision could be made between the two processes.

TABLE V

Distribution of Phenolic By-Products between Aqueous Phosphate and Organic Solvent

By-products in aqueous phase g/l	By-products in MIBK g/l	By-products in aqueous phase g/l	By-products in Benzene g/l
6.84	1.98	6.10	1.18
5.44	1.38	5.27	0.83
4.43	1.02	4.67	0.60
3.58	0.85	3.20	0.36
2.86	0.65	1.96	0.15
2.32	0.54		
1.40	0.28		

Conclusions

The main conclusions of this investigation are:-

1. The principal by-products formed during the mixed-acid mononitration of toluene are nitrous acid and nitrated phenolic compounds, of which 2, 6 dinitro p-cresol constitutes about 80%.
2. Nitrous acid and the organic acids by-product are formed in equimolar quantities, within experimental error.
3. The ratio of by-products to mono-nitrotoluene is reduced if the sulphuric acid concentration in mixed acid is a high as possible although still below the concentration at which di-nitration commences. Increase in sulphuric acid concentration from the normal 30 mole % to 35 mole % decreases organic by-products by over 25%.
4. Nitro-phenolic compounds and nitrous acid are similarly formed during the nitration of other aromatic hydrocarbons. Of those studied, the order from highest to lowest in proportion of by-products to mono-nitro product was:- o-xylene, p-xylene, toluene, ethyl benzene, mesitylene, m-xylene, benzene.
5. For removal of the nitro-phenolic by-products, a process of dissociation extraction using a mixture of phosphate salts is viable and could be conomically preferable to simple solvent extraction by an organic solvent.

Literature Cited

1. Neolting,E. and Forel,S., Ber. (1885) 18, 2670
2. Noelting,E. and Pick,B., Ber. (1889) 21, 3158
3. Armstrong,H.E. and Rossiter,E.C., J.Chem.Soc.Proc.(1891) 7,89
4. Berkenheim,A.M. and Coster,M.I., J.Gen.Chem.USSR (1933) 3,385
5. Titov,A.I. and Barysnikova,A.N., Zh.Obschch.Khim.USSR (1936) 6,1801
6. Titov,A.I. U.S.P. Khim (1958) 27,845

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

7. Bennett,G.M. and Youle,P.V.,J.Chem.Soc.(1938) 887
8. Bennett,G.M. and Youle,P.V.,Nature (1938) 142,356
9. Bennett,G.M. and Youle,P.V.,J.Chem.Soc. (1938) 1816
10. Dadak,V. and Seitl,J.,J.Chem.Prumsyl.(1959) 88,276
11. Dadak,V.,Seitl,J. and Smejkal,K.,Chem.Prumsyl.(1962) 12,69
12. Dadak,V. and Seitl,J.,Chem.Prumsyl.(1962) 12,352
13. Dadak,V.,Smejkal,K. and Balasova,E.,Chem.Prumsyl.(1963) 13,241
14. Sohrabi,T.(née Kaghazchi),PhD Thesis, University of Bradford (1972)
15. Olah,G.A.,Kuhn,S.J.,Flood,S.H. and Evans,J.C.,J.Amer.Chem. Soc.(1962) 84,3687
16. Bennett,G. and Grove,J.F.,J.Chem.Soc.(1945) 378
17. Bennett,G.M.,J.Proc.Roy.Inst.Chem.(1943) 107
18. Titov,A.I.,Zhur.Obshchei.Khim.(J.Gen.Chem.) (1952) 22,1329
19. Coombes,R.G., Department of Chemistry, The City University, London, private communication
20. Blackstock,D.J. et al, Tet.Letters,(1970) 2793
21. Barnett,J.W.,Moodie,R.R.,Schofield,K. and Weston,J.B., J.C.S. Perkin II (in the press)
22. Anwar,M.M.,Hanson,C. and Pratt,M.W.T.,Proc.ISEC(1971) 911, Academic Press (London)
23. Anwar,M.M.,Cook,S.T.M.,Hanson,C. and Pratt,M.W.T., Proc. ISEC (1974),Vol.1, 895, SCI(London)

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch008

9

Nitric Acid Oxidations

NORMAN C. DENO

The Pennsylvania State University, University Park, Pa. 16802

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch009

The common mechanism for nitration of aromatic hydrocarbons consists of replacement of H^+ by $NO_2{}^+$ and in this process, oxidation-reduction plays no part. However, there are reactions of nitric acid and its reduction products that do produce nitro compounds and do involve complex oxidations and reductions. Examples are (a) the conversion of alkanes to smaller nitroalkanes via fragmentations, (b) the conversion of alkanes to nitroalkanes, (c) the nitration of anisole in which nitrosation and oxidation of the nitroso to nitro can be very much faster than direct nitration,(1) (d) the oxynitration of benzene to 2,4-dinitrophenol in the presence of Hg(II), and (e) the additions to double bonds to form a confusing variety of nitro and nitroso compounds and nitrites and nitrates.

Several circumstances transpire to effect an atmosphere of uncertainty about most of these reactions. Much of the work dates back before the days of gc and nmr and a significant fraction is over 50 years old. Furthermore, a large body of the work is in Russian. Noteworthy are the extensive studies of Titov which were reviewed by Titov,(2) but just before Usp. Khim. began to be translated into English. Fortunately, there is one excellent review of most of the work in English and that is in a book by Sosnovsky.(3) Finally, the systems themselves are enormously complex with HNO_3, N_2O_5, HNO_2, N_2O_3, NO, and N_2O all present and all able to function as oxidizing agents.

Recently, we have completed some studies on the oxidation of carboxylic acids and alcohols which suggest that the mechanism of oxidation of acids is very different than that of alcohols. Both oxidations are conducted with 70% aqueous HNO_3 at 90-100° under good stirring. The oxidation of carboxylic acids will be considered first.

When hexadecanoic (palmitic) acid is oxidized with 70% HNO_3, a mixture of predominantly C_{11}-C_{15} dicarboxylic acids is produced first, (Table I).(4) This is only evident at low conversions (10%) because these diacids undergo further oxidation. A noteworthy aspect of the reaction is that products that would

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch009

Table I. Products from Oxidation of Palmitic (C_{16}) Acid with 70% HNO_3 (105-110°)

Diacid of Carbon Number	Wt. % Diacid	
	10% Conversion^a	100% Conversion^a
4	0	2
5	1	3
6	2	8
7	3	18
8	4	21
9	8	21
10	12	13
11	14	7
12	16	3
13	16	3
14	14	1
15	10	0
16	0	0

(a) From ref. 4 (b) These differ somewhat from values in ref. 4 because of a shorter reaction time and slightly higher T.

arise by oxidation at the carboxyl end of the molecule (C_{15}, C_{14}, etc. monoacids) are never present.(4) Not only is the carboxyl group and its environs inert to the oxidation, but the oxidation is not significant on CH_2 groups until they are 8-10 carbons removed from the carboxyl group.

The oxidation is thus essentially the oxidation of an alkane. Titov had shown in the oxidation of alkanes that no reaction occurs in the absence of NO_2 and that the first step is abstraction of a H atom by NO_2.(2,3) Similarly the oxidation of carboxylic acids fails if urea is present to destroy NO_2.

Having established that initial attack is by NO_2, it is of interest to draw a parallel between the oxidations in Table I and chlorinations by R_2NCl.(5) In both cases electronegative groups strongly repel the attacking reagent, NO_2 and $R_3N^{\dot{+}}$ respectively, and to a degree without precedent in synthetic organic chemistry. In both cases the attacking reagent is a free radical with the unpaired electron on N or potentially on N and the N is substituted by powerfully electron-withdrawing groups. The factors responsible for the great polar selectivity in the HNO_3 oxidation of carboxylic acids can be assumed to be the same as those attributed to the R_2NHCl^+ and R_3NCl^+ chlorinations.(5)

At 100% conversion, the products are largely C_6-C_{10} dicarboxylic acids (Table I). These form because the C_{11}-C_{15} diacids are oxidized at the midpoint in the chain. A necessary consequence of this path is that MW is augmented and the weight of products is more (~10%) than the weight of the reactant. This is observed.(4) The C_6-C_{10} diacids are relatively inert to further oxidation because all CH_2 groups are now within 4-5 carbons of a carboxyl group. A variety of other carboxylic acids have been oxidized by HNO_3 and the products are in accord with the above principles.

These nitric acid oxidations in the liquid state contrast sharply with oxidations in the vapor state. The reaction of alkanes with HNO_3 or NO_2 at 150-220° gives nitroalkanes.(2,3,6-8) The liquid state oxidations produce only trace amounts of $C\text{-}NO_2$ compounds as shown by the infrared spectra.

Alcohols are rapidly oxidized by HNO_3, and the reaction is complete in an hour at 90°. Products from four representative cases are shown in Table II.

Table II. Products from HNO_3 Oxidation of Alcohols at 90°

Substrate	% Yield of RCOOH of Carbon Number[a]				
	5	6	7	8	9
1-octanol	0	8	56	36	-
2-octanol	0	68	32	0	-
1-nonanol	0	0	10	65	25
	% Yield of $HOOC(CH_2)_nCOOH$ of Carbon Number				
	8	9	10	11	12
12-hydroxystearic acid	0	0	9	41	50

(a) Analyzed by gc of methyl esters.

These oxidations of alcohols are not believed to involve H abstraction by NO_2. The parallel behavior of R_3N^{+} and NO_2 has already been noted in the remote attack on carboxylic acids. Since the alcohol function is inert to R_3N^{+}(5), it is presumed that it would also be inert to NO_2. This suggests that the oxidation of alcohols by HNO_3 is an ionic reaction involving an internal breakdown of a nitrate ester.

One curious aspect of the HNO_3 oxidation of alcohols is that a small amount of allylic oxidation accompanies the normal oxidation. For example, oxidation of 12-hydroxystearic acid produces some C_{10} diacid along with the expected C_{11} and C_{12} diacid (Table II). At one time this might have been ascribed to oxidation at the $\alpha\text{-}CH_2$ to degrade the acid to its next lower homolog, but the results on the oxidation of palmitic acid and other monoacids completely disprove such a possibility. One viable possibility is that the ketone or aldehyde is an intermediate and that some oxidation takes place on the allylic position of the enol form. In any event, this allylic oxidation is an inherent part of the mechanism and not a subsequent oxidation of the carboxylic acid once it has formed.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch009

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Acknowledgment. This work was supported by grants from the Fats and Proteins Research Foundation and the National Science Foundation. This support is gratefully acknowledged.

Literature Cited

(1) Deno, N., and Stein, R., J. Amer. Chem. Soc., 78, 578 (1958).

(2) Titov, A., Usp. Khim., 21, 881 (1952); 27, 845 (1958).

(3) Sosnovsky, G., "Free Radical Reactions in Preparative Organic Chemistry," The MacMillan Co., New York, 1964, chapter VII.

(4) Deno, N., Pierson, C., and Seyhan, S., J. Amer. Chem. Soc., 95, 6857 (1973).

(5) Deno, N. in "Methods in Free Radical Chemistry," Ed. E. Huyser, Dekker and Co., New York, 1972, vol. 3, chapter 3; Deno, N., Billups, W. E., Fishbein, R., Pierson, C., Whalen, R., and Wyckoff, J. C., J. Amer. Chem. Soc., 93, 438 (1971).

(6) Asinger, F., Chem. Ber., 77, 73 (1944).

(7) Geiseler, G., Angew. Chem., 67, 270 (1955).

(8) Spaeth, C., U.S. patents 2,883,432; 2,883,433; and 2,883,434; Chem. Abstr., 53, 16025 (1959).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch009

10

The Alkyl Nitrate Nitration of Active Methylene Compounds

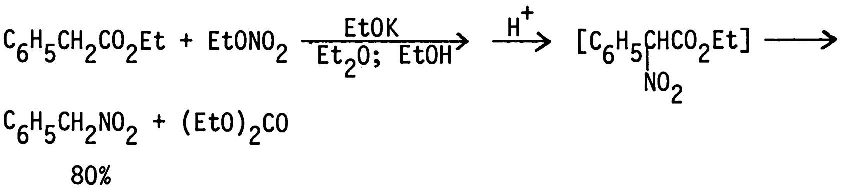
HENRY FEUER

Department of Chemistry, Purdue University, West Lafayette, Ind. 47907

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

The nitration of active methylene compounds by the action of a nitrate ester under basic conditions has been found to be a general and convenient method for introducing a nitro group alpha to the activating group. By choosing the appropriate base-solvent system, we have been successful in applying the reaction to ketones, nitriles, amides, carboxyl esters, sulfonic esters, sulfones, substituted toluenes, and heterocyclics. Usually the nitration under acidic conditions fails with these classes of compounds.

The reaction goes back to the turn of the century (1). Wislicenus (2) applied it to phenylacetic esters (eq 1). The re-

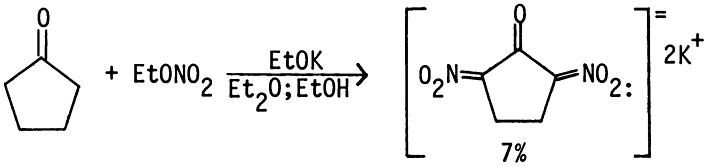


$$C_6H_5CH_2CO_2Et + EtONO_2 \xrightarrow[Et_2O;\ EtOH]{EtOK} \xrightarrow{H^+} [C_6H_5\underset{NO_2}{C}HCO_2Et] \longrightarrow C_6H_5CH_2NO_2 + (EtO)_2CO \qquad (1)$$

80%

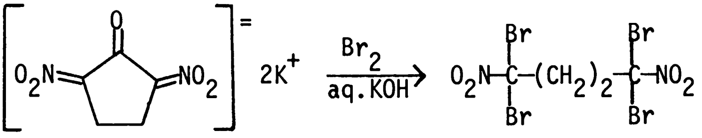
action led to phenylnitromethane in high yield and is still one of the best methods for preparing this compound. The crude reaction product was treated directly with hydrochloric acid. None of the nitro ester was obtained. Wislicenus was unsuccessful to extend the reaction to simple aliphatic esters. This is not surprising because the base-solvent system employed was not strong enough to convert these esters to their anions.

About 28 years later, Wieland (3) applied essentially Wislicenus' method to the nitration of cyclic ketones. The reaction with cyclopentanone gave the dipotassium salt of α, α'-dinitrocyclopentanone in a reported yield of 75% (eq 2). The yield and purity of the salt was based on a potassium analysis only. We found that the yield of the disalt was about 10% and that most of the starting material was lost in the formation of tar (4).



(2)

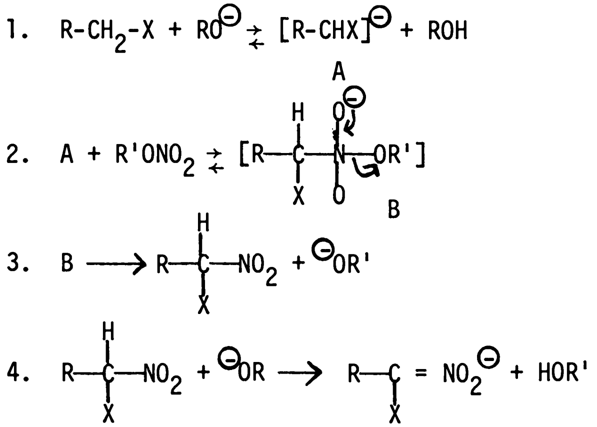
The yield of nitration was determined by a ring opening reaction (5) in which the dinitro salt is converted to 1,1,4,4-tetrabromo-1,4-dinitrobutane (eq 3). The ring opening which is essentially a haloform reaction has been established to proceed in a yield of about 85%.



(3)

The outcome of this investigation indicated that in order to improve the yield a stronger base than ethoxide must be used and that the solvent should be aprotic. The accepted mechanism of the reaction, shown in Scheme 1 bears this out. The first step in the

Scheme 1



1. $R\text{-}CH_2\text{-}X + RO^{\ominus} \rightleftarrows [R\text{-}CHX]^{\ominus} + ROH$ (A)

2. $A + R'ONO_2 \rightleftarrows [R-\overset{H}{\underset{X}{C}}-\overset{O^{\ominus}}{\underset{O}{N}}-OR']$ (B)

3. $B \longrightarrow R-\overset{H}{\underset{X}{C}}-NO_2 + {}^{\ominus}OR'$

4. $R-\overset{H}{\underset{X}{C}}-NO_2 + {}^{\ominus}OR \longrightarrow R-\underset{X}{C}=NO_2^{\ominus} + HOR'$

X = Activating group

reaction involves the removal of an acidic hydrogen from the alpha carbon by the base. The resulting resonance stabilized carbanion A then undergoes a nucleophilic attack on the nitrate ester to give intermediate B in step 2. This intermediate collapses, as shown in step 3, into the nitro compound and alkoxide. Then the alkoxide or any other base present converts the nitro compound, in step 4, to the nitronate salt. The latter can then be converted to the nitro compound in a suitable acidification step.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Consideration of this mechanism makes it clear that for a successful reaction important requirements have to be met. (1) The generation of a high concentration of anion by the choice of a strong base. (2) Reaction conditions must be found which would minimize interaction between the base and nitrating agent and also side reactions of the substrate such as self-condensation of ketones.

The choice of sublimed potassium t-butoxide free of t-butyl alcohol in peroxide-free tetrahydrofuran (THF) was found to be a suitable base for the nitration of aliphatic and cyclic ketones, nitriles (6) and N-disubstituted amides (7). As the nitrating agent, primary alkyl nitrates such as ethyl nitrate were chosen, after it was established that they were not affected by the base, t-butoxide below -10°.

The importance of the right solvent is shown in Table I. In a study with cyclopentanone the highest yield was obtained in THF in which sublimed K t-butoxide is soluble to the extent of 25% at 25-26°. But even in hexane in which K t-butoxide is only sparingly soluble the yield was 38%. It should be recalled that the yield was only 7% when the base-solvent system was potassium ethoxide in a mixture of ether and ethyl alcohol.

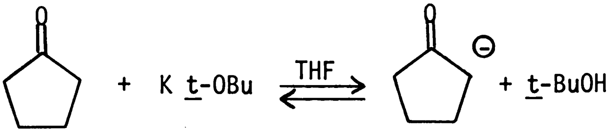
Table I

SOLVENT EFFECTS IN THE ALKYL NITRATION OF CYCLOPENTANONE

SOLVENT	SOLUBILITY OF Kt-OBu[a]	% YIELD[b]
Toluene	2.27	21
Hexane	0.27	38
Ether	4.34	55
THF	25.00	62

[a] In g/100g solvent at 25-26°. [b] Determined by conversion of dipotassium 2,5-dinitrocyclopentanone to $O_2NBr_2C-(CH_2)_2-CBr_2NO_2$

The advantage of sublimed potassium t-butoxide lies not only in its being a strong base but also in its ability to bind strongly one equivalent of t-butyl alcohol which is formed in the carbanion formation (eq 4). The removal of the alcohol ensures a favorable equilibrium for carbanion formation. The adverse effect of added t-butyl alcohol on the yield of nitro compound is shown in Table II. The amount of alcohol which was added is only 1.5



(4)

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

times larger than the amount of t-butyl alcohol formed in the reaction. It can be seen that an excess of base gave higher yields; the optimum was found to be a 65% excess of base. Even the presence of a hydroxyl group in a molecule was found to be deleterious for the nitration. Schaub (8) reported that by using our reaction conditions in the nitration of testosterone, the yield of 2-nitrotestosterone was only 9%. When the hydroxyl group was converted to the tetrahydropyran ether, the yield was increased to 42%.

Table II
EFFECT OF ADDED t-BuOH ON THE ALKYL NITRATION OF CYCLOPENTANONE

KETONE	K t-OBu	t-BuOH	% YIELD
0.05	0.110	0.00	39.0
0.05	0.110	0.11	15.5
0.05	0.165	0.00	55.0
0.05	0.165	0.15	17.0

The reaction conditions which led to high yields of nitro compounds are as follows: potassium t-butoxide (65% excess) is added to purified THF and the mixture cooled to about -40°. Then the compound dissolved in THF is added followed by the dropwise addition of nitrate (10% excess) at -40° to -50°. The nitro salt formed is then removed by filtration after room temperature is attained.

The results with cyclic ketones are shown in Table III. The yields are based in the case of cyclic ketones on the bromination products the 1,1,4,4-tetrabromo-1,4-dinitroalkanes, and in the case of α-tetralone on 2-(3,3-dibromo-3-nitropropyl)benzoic acid, which resulted from ring cleavage. The results with aliphatic ketones are shown in Table IV. No efforts were made to optimize the yields.

Table III
ALKYL NITRATION OF CYCLIC KETONES

KETONE	% YIELD[a]
Cyclopentanone	75
Cyclohexanone	55
Cycloheptanone	55
Cyclooctanone	35
α-Tetralone	40[b]

[a] Determined by conversion to $O_2NBr_2C-(CH_2)_n-CBr_2NO_2$.

[b] Determined by conversion to o-$O_2NBr_2C-(CH_2)_2-C_6H_4CO_2H$.

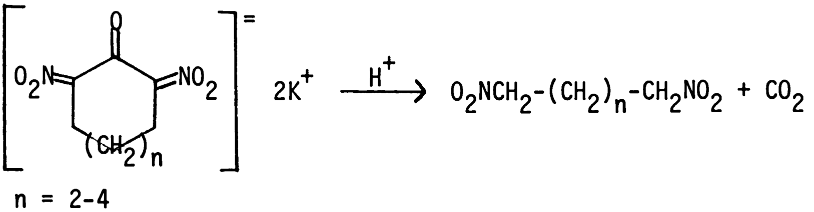
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Table IV

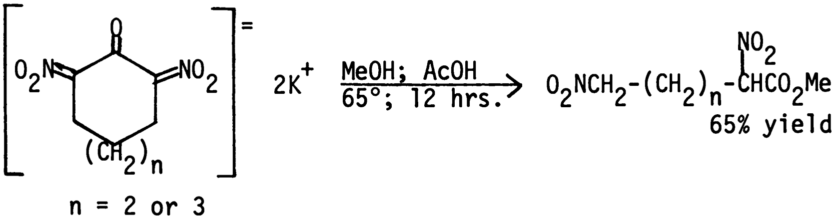
KETONE	NITRATION PRODUCT	% YIELD
4-Heptanone	Dipotassium 3,5-Dinitro-4-heptanone	50.5*
Butanone	Dipotassium 1,3-Dinitrobutanone	57
Acetone	Dipotassium 1,3-Dinitropropanone	49
Acetophenone	Potassium w-Nitroacetophenone	40.5

*Based on 3,5-dibromo-3,5-dinitro-4-heptanone.

The importance (9) of the salts of α,α'-dinitrocyclanones is indicated by their facile conversion in high yield to α,w-dinitroalkanes (eq 5). The method is superior to the well known Victor Meyer reaction in which halogen compounds are treated with silver nitrite. When the ring opening reaction is performed in refluxing methanolic acetic acid, no decarboxylation occurs. Instead α,w-dinitroalkylcarboxylic methyl esters are obtained (eq 6).

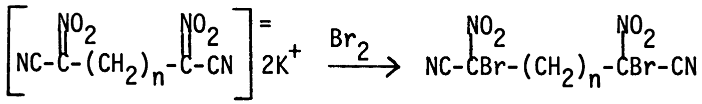


(5)



(6)

The results with nitriles are shown in Table V. The yields of these nitration reactions were determined by converting the salts of the α-nitroalkylnitriles to the corresponding α-bromo-α-nitroalkylnitriles (eq 7). Although the free α-nitroalkylnitriles are unstable at room temperature, the salts can be used



$$\left[NC-\overset{NO_2}{\overset{\|}{C}}-(CH_2)_n-\overset{NO_2}{\overset{\|}{C}}-CN\right]^{=} 2K^+ \xrightarrow{Br_2} NC-\overset{NO_2}{\overset{|}{C}}Br-(CH_2)_n-\overset{NO_2}{\overset{|}{C}}Br-CN \qquad (7)$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

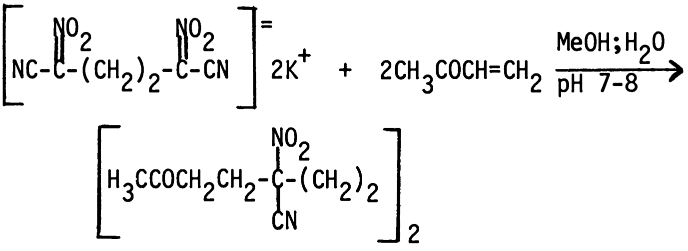
Table V

ALKYL NITRATION OF NITRILES

NITRILE	BROMO NITRO NITRILE % YIELD*
Adiponitrile	78
Pimelonitrile	45
Suberonitrile	67
Sebaconitrile	48
Butanenitrile	44
Hexanenitrile	55

*Based on the starting nitrile

directly in further reactions. As an example, dipotassium α-α'-dinitroadiponitrile reacted readily in a Michael type reaction with methyl vinyl ketone to give the diadduct 5,8-dicyano-5,8-dinitro-2,11-dodecanedione (eq 8).



$$\left[\mathrm{NC}\text{-}\overset{\mathrm{NO_2}}{\overset{\|}{\mathrm{C}}}\text{-}(\mathrm{CH_2})_2\text{-}\overset{\mathrm{NO_2}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{CN}\right]^{=} 2\mathrm{K}^+ + 2\mathrm{CH_3COCH{=}CH_2} \xrightarrow[\mathrm{pH}\ 7\text{-}8]{\mathrm{MeOH;H_2O}} \left[\mathrm{H_3CCOCH_2CH_2}\text{-}\underset{\mathrm{CN}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\text{-}(\mathrm{CH_2})_2\right]_2 \qquad (8)$$

51% yield

The t-butoxide-THF system gave good results in the alkyl nitrate nitration of active methylene compounds in the approximate acidity range of 18-25 pka units. Application of this base-solvent system to compounds of lower acidity such as substituted toluenes, aliphatic carboxylic esters, aliphatic sulfonic esters and heterocyclics gave nitro compounds in very low yield or was completely unsuccessful. Therefore we investigated whether a stronger base such as potassium amide or sodium amide in liquid ammonia could be used as the base-solvent system in the alkyl nitrate nitration. In control experiments it was found that at the liquid ammonia temperature, an exotherm developed when the alkyl nitrate was added to the base and that there was interaction between these two components. So the question arose whether these two factors could be controlled. The data shown in Table VI show that in the amide-ℓ.ammonia system the nitration of cyclanones gave as good or better results than in the K t-OBu-THF system (10). In regard to the nitration of cycloheptanone, the dinitro salt obtained in the K t-OBu-THF system could not be purified while the product obtained in the $\mathrm{KNH_3}$-ℓ.$\mathrm{NH_3}$ system could be

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

readily purified and the yield was 85%. Best results were obtained when the ratio of substrate to amide to nitrate was 1:2:2.5.

Table VI

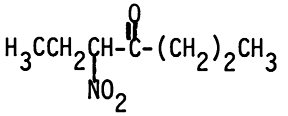
DINITRATION OF CYCLANONES IN K *t*-OBu-THF AND KNH_2-ℓ.NH_3

KETONE	DISALT K *t*-OBu-THF % YIELD	DISALT KNH_2-ℓ.NH_3 % YIELD
Cyclopentanone	98	94
Cyclohexanone	75	95
Cycloheptanone	-	85

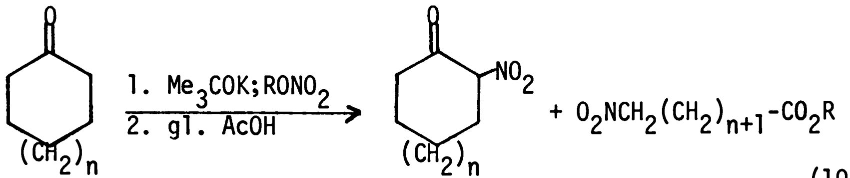
Regarding the control of the temperature it was observed that the exotherm ceased after addition of the first drops of the nitrate to the reaction mixture. Afterwards the nitrate could be added at a fast rate. The experimental procedure is simple and is as follows: the ketone is added to potassium amide in liquid ammonia at -33° and the suspension stirred for 30 min. Then the nitrate ester is added dropwise over 10 min, the mixture stirred for 30 min, and the ammonia gradually replaced by ether. Filtration gives then the nitro salt.

In the alkyl nitration of ketones only one alpha hydrogen is replaced by the nitro group when equimolar amounts of base and ketone are employed. However, in the case of aliphatic ketones, mononitration is accompanied by a fragmentation reaction (11). Thus the nitration of 4-heptanone affords 3-nitro-4-heptanone, 1-nitropropane and ethyl butyrate (eq 9). In the case of cyclic ketones mononitration leads to *α*-nitrocyclanones and to *w*-nitroalkyl esters (eq 10).

$$(CH_3CH_2CH_2)_2CO \xrightarrow[AmONO_2]{KNH_2\text{-}\ell.NH_3} \xrightarrow{H^+} H_3CCH_2CH_2CO_2Et + H_3CCH_2CH_2NO_2 + \quad (9)$$



$$H_3CCH_2\underset{NO_2}{\underset{|}{C}}H\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2CH_3$$



(10)

n = 3,4,5,6,7 or 9.
R = Alkyl.

The relative amounts in which these products are formed is a function of ring size and also of the base-solvent system used in the alkyl nitration. A comparison of the results of mononitration of cyclic ketones in the KNH_2-ℓ.NH_3 (10) and K t-OBu-THF systems (11) is presented in Table VII. In both systems the amount of ring cleavage increases in the middle ring region. However, it is of interest that less ring cleavage occurs in the KNH_2-ℓ.NH_3 system and also that the total amount of nitration is increased.

Table VII

COMPARISON OF THE RESULTS OF MONONITRATION OF KETONES IN THE KNH_2-ℓ.NH_3 and K t-OBu-THF SYSTEMS

	α-Nitroketone		w-Nitrocarboxylic Ester	
Ketone	THF	NH_3	THF	NH_3
Cyclohexanone	20	59	10	2
Cycloheptanone	65	79	4	1
Cyclooctanone	35	60	37	21
Cyclononanone	14	26	60	45
Cyclodecanone	14	17	58	49
Cyclododecanone	54	64	23	17

The importance of the base to alkyl nitrate ratio on the mononitration of cyclanones in the KNH_2-ℓ.NH_3 system is shown in Table VIII. A 2:1 ratio of nitrating agent to base is essential to obtain high yields.

Table VIII

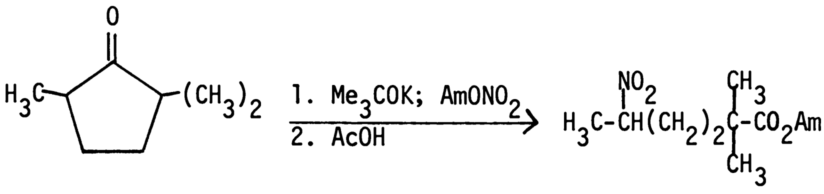
EFFECT OF ALKYL NITRATE TO BASE RATIO ON THE MONONITRATION OF CYCLOALKANONES IN THE KNH_2-ℓ.NH_3 SYSTEM

Ketone*	BASE equiv	ALKYLNITRATE equiv	α-NITROKETONE yield, %
CYCLOHEPTANONE	1	1.1	62
"	2	1.1	3
"	1	2.0	79
CYCOOCTANONE	1	1.1	54
"	1	2.0	60

*In all expts. the ketone was stirred for 2 hr at -33° in the basic solution before the nitrate was added.

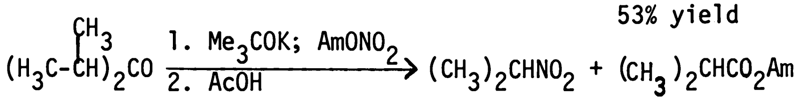
In the case of α,α'-disubstituted ketones where nitration would lead to tertiary nitroketones, cleavage is the prevalent reaction. Two examples are shown in eqs 11 and 12. The fact that in these cases nitroketones, which would be tertiary are not formed, indicates that there is a competition between the pathways leading to uncleaved and cleaved products. In a rather detailed investigation (11) we established that these competitive

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010



(11)

53% yield

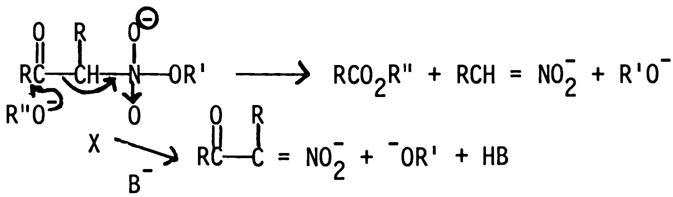


$$(H_3C\text{-}\overset{CH_3}{CH})_2CO \xrightarrow[2.\ AcOH]{1.\ Me_3COK;\ AmONO_2} (CH_3)_2CHNO_2 + (CH_3)_2CHCO_2Am \qquad (12)$$

66% yield 84% yield

reactions occur during the nitration reaction and that the intermediate X shown in Scheme 2 must participate. Alkoxide attack

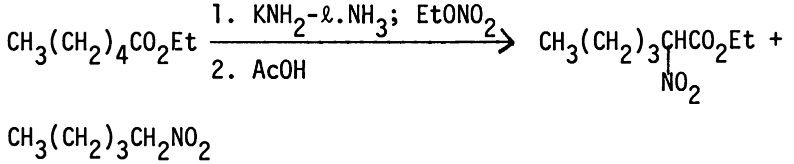
Scheme 2



at the carbonyl group of intermediate X which may have some stability at -40° leads to the fragmentation reaction. The same intermediate could also lead to the nitroketone after abstraction of the alpha hydrogen by base such as K *t*-OBu.

The amide-ℓ.ammonia system made it possible to extend the alkyl nitrate nitration to weak acidic systems such as aliphatic carboxylic esters, alkylsulfonates, to aromatics with electron withdrawing groups and to heterocyclics.

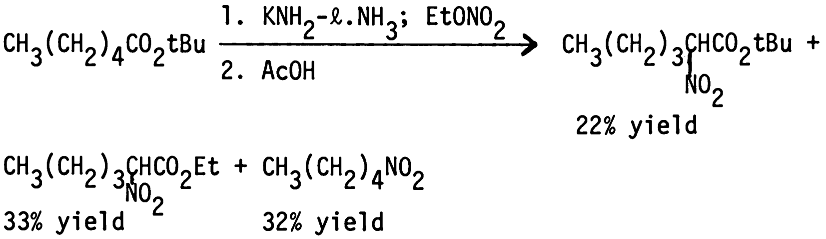
The results with esters is discussed next. The nitration of ethyl caproate gave 42% of the nitro ester and also 13% of 1-nitropentane and of diethyl carbonate resulting from a decarboxylation reaction (eq 13). The total amount of nitration amounted to 55% and 25% of unreacted ester was recovered when a 10% excess of base was used. When a larger excess of amide was used to in-



$$CH_3(CH_2)_4CO_2Et \xrightarrow[2.\ AcOH]{1.\ KNH_2\text{-}\ell.NH_3;\ EtONO_2} CH_3(CH_2)_3\underset{NO_2}{CH}CO_2Et + CH_3(CH_2)_3CH_2NO_2 \qquad (13)$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

crease anion formation, ammonolysis of the ester interfered with the nitration reaction. In order to avoid this difficulty t-butyl esters were chosen because amide formation was found to be negligible even with a 100% excess of KNH_2 (12). In the case of t-butyl caproate the total nitration was increased from 55% to 87% and 5% of the ester was recovered. In addition to the t-butyl nitrocaproate and the expected fragmentation products, there was formed another ester namely ethyl nitrocaproate (eq 14). The ethyl group came of course from the nitrating agent, ethyl nitrate. The results of nitration of various t-butyl and ethyl



$$CH_3(CH_2)_4CO_2tBu \xrightarrow[\text{2. AcOH}]{\text{1. } KNH_2\text{-}\ell.NH_3\text{; } EtONO_2} \underset{\text{22\% yield}}{CH_3(CH_2)_3\underset{NO_2}{C}HCO_2tBu} + \underset{\text{33\% yield}}{CH_3(CH_2)_3\underset{NO_2}{C}HCO_2Et} + \underset{\text{32\% yield}}{CH_3(CH_2)_4NO_2} \qquad (14)$$

esters are shown in Table IX. In all cases the over-all nitration is higher with t-butyl esters and more of the transesterified ester is formed, except in the case of t-butyl phenylacetate, where the major product is phenylnitromethane arising from the fragmentation reaction.

Table IX

ALKYL NITRATE NITRATION OF ETHYL AND t-BUTYL ESTERS

RCH_2CO_2R'		$RCHNO_2CO_2Et$	$RCHNO_2CO_2t\text{-}Bu$	RNO_2	Total Nitration[a,b]
R	R'	Yield %	Yield %	Yield %	Yield %
Et	Et	41	--	14	55
Et	t-Bu	31	23	25	79
Bu	Et	42	--	14	56
Bu	t-Bu	33	22	33	88
C_6H_5	Et	23	--	49	72
C_6H_5	t-Bu	4	36	49	89

[a] Nitrations were carried out in $KNH_2\text{-}\ell.NH_3$ at -33° with ethyl nitrate. [b] Total nitration represents the sum of t-butyl and ethyl α-nitro esters, and nitroalkane.

The importance of the acidity of the starting ester on the success of the alkyl nitration is indicated in Table X. The highest yield of over-all nitration was realized with the least acidic ethyl p-methoxyphenylacetate and no nitration with ethyl p-nitrophenylacetate. Diethyl malonate and diethyl methylmalonate also failed to undergo nitration. These results seem to indicate that in the $KNH_2\text{-}\ell.NH_3$ system only compounds with pK_a

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Table X

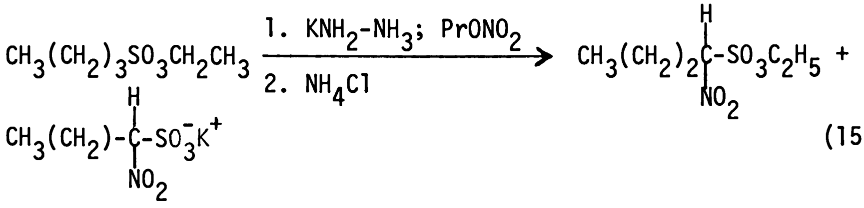
DEPENDENCE OF THE ACIDITY OF ESTERS ON THE SUCCESS OF THE ALKYL NITRATION

RCH_2CO_2Et	$RCHNO_2CO_2Et$	RNO_2
R	% Yield	% Yield
C_6H_5	23	49
p-$MeOC_6H_4$	72	22
p-$NO_2C_6H_4$*	0	0

*75% of ester was recovered.

greater than 16 would undergo nitration. In the second step of the proposed mechanism of the reaction as illustrated in Scheme 1 the reaction between ester anion and alkyl nitrate is reversible, and with carbanions of acidic esters the position of the equilibrium lies far to the left.

In contrast to the carboxylic esters, no transesterification or desulfonation (cleavage of the C-S bond) is observed, in the alkyl nitration of alkylsulfonate esters. Ethyl butanesulfonate is converted to ethyl α-nitrobutanesulfonate (54%) and the potassium salt of α-nitrobutanesulfonic acid (11%), about 33% of the ester being recovered (eq 15). The salt of α-nitrobutanesulfonic acid arises from a β-elimination with the loss of ethylene (13).



$$CH_3(CH_2)_3SO_3CH_2CH_3 \xrightarrow[2.\ NH_4Cl]{1.\ KNH_2\text{-}NH_3;\ PrONO_2} CH_3(CH_2)_2\overset{H}{\underset{NO_2}{C}}\text{-}SO_3C_2H_5 + CH_3(CH_2)\text{-}\overset{H}{\underset{NO_2}{C}}\text{-}SO_3^-K^+ \qquad (15)$$

To avoid the β-elimination neopentyl alkylsulfonates were subjected to the alkyl nitration. The results summarized in Table XI indicate that the yields of nitration decrease with lengthening of the chain. To obtain optimun yields of α-nitrosulfonate esters containing 8-12 carbons in the chain more concentrated reaction mixtures had to be employed (instead of 250 ml, only 100 ml of liquid ammonia was used). In the case of the C_{12}-sulfonate the yield was only 3% when the nitration was carried out in 250 ml of liquid ammonia. The yield increased ten-fold to 33% when the reaction was performed in only 100 ml of ammonia. It is likely that the low yield was due to a slower rate of anion formation. In fact the yield was increased from 33% to 47% when the anion of the C_{12}-sulfonate was generated with KNH_2 in THF at 65° and then nitrated at -40°. The C_{16}-sulfonate did not undergo nitration at all. This was due to a lack of anion formation. Even when the compound was treated with KNH_2 in THF at 65°, no deuterium was

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Table XI

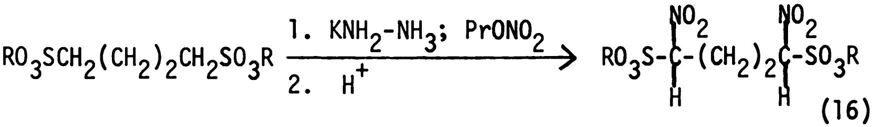
ALKYL NITRATE NITRATION OF NEOPENTYL SULFONATE ESTERS

$RSO_3CH_2C(CH_3)_3$	Neopentyl 1-nitrosulfonate ester Yield, %[a]	Yield, %[b]
CH_3CH_2–	73.8 (22.2)[c]	
n-C_4H_9–	75.5 (22.2)	75.6 (20.2)
n-C_6H_{13}–	55.8 (36.7)	75.2 (20.8)
n-C_8H_{17}–	32.8 (61.6)	75.6 (21.7)
n-$C_{10}H_{21}$–	16.9 (78.1)	55.7 (39.7)
n-$C_{12}H_{25}$–	3.0 (93.4)	33.9[d] (62.7)
n-$C_{16}H_{33}$–	0 (95.7)	0 (95.5)
$CH_3CH_2CH(CH_3)$–		34.7 (59.8)

[a] Reactions were carried out with potassium amide in 250 ml of liquid ammonia at -33°. The nitration time was 5 min. [b] Reactions were carried out with potassium amide in 100 ml of liquid ammonia at -33°. [c] The numbers in parenthesis represent recovered starting material. [d] The yield was 47.0% when anion formation was carried out with potassium amide in THF at 65°, and the nitration at -33°.

introduced on quenching in D_2O.

The nitration was also successful with a disulfonate ester as shown in eq 16.



$$RO_3SCH_2(CH_2)_2CH_2SO_3R \xrightarrow[2.\ H^+]{1.\ KNH_2\text{-}NH_3;\ PrONO_2} RO_3S\text{-}\overset{NO_2}{\underset{H}{C}}\text{-}(CH_2)_2\overset{NO_2}{\underset{H}{C}}\text{-}SO_3R \quad (16)$$

R = Neopentyl 69% yield

The results of nitration of several activated toluenes are shown in Table XII. It is of interest that the yield of nitro compound is dependent on the activating group. Moreover with two substituted toluenes, higher yields were realized in the weaker basic $NaNH_2$-ℓ.NH_3 system than in the stronger KNH_2-ℓ.NH_3 system. While in the case of p-cyanotoluene the yield of p-cyanophenylnitromethane was comparable in both systems, 4-methylbenzophenone underwent nitration only in the KNH_2-ℓ.NH_3 system and the yield of p-benzoylnitromethane was only 16%. On the other hand N,N-dimethyl-p-toluenesulfonamide and phenyl p-tolyl sulfone gave much higher yields of the corresponding nitro compounds with $NaNH_2$ than with KNH_2 (14).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Table XII

ALKYL NITRATE NITRATION OF ACTIVATED TOLUENES

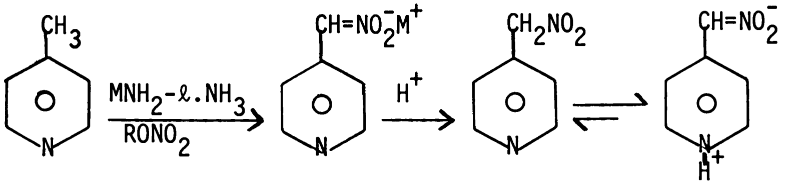
$X\text{-}C_6H_4CH_3$ X	Arylnitromethane Yield, %	$X\text{-}C_6H_4CH_3$ Recovery, %
p-CN-	46.6 (42.3)	41.5 (36.3)
o-CN-	38.3	35.0
p-$C_6H_5C{=}O$	16.0 (none)	64.0 (100)
p-Me_2NSO_2-	14.9 (40)	55.3 (27.1)
p-$C_6H_5SO_2$-	4.1 (54.7)	84.0 (39.2)

The numbers in () refer to results in the $NaNH_2\text{-}NH_3$ system.

We also were successful in applying the alkyl nitrate nitration to π-deficient heterocyclic compounds such as 2- and 4-methylpyridines, 4-methylpyrimidine, and to π-excessive heterocyclics such as 2-methylbenzoxazole and 2-methylbenzothiazole (15). Both sodium and potassium amides in liquid ammonia were found to be effective as bases. In the $KNH_2\text{-}\ell.NH_3$ system optimum yields are obtained if the molar ratio of base to substrate to nitrate ester is 2.0:1.0:2.5. After allowing 2-3 minutes for anion formation the nitrate ester is added as rapidly as possible while maintaining the temperature below -33°. Next the ammonia is replaced with ether and the nitro salt filtered off and acidified with aqueous acetic acid.

In the weaker basic $NaNH_2\text{-}\ell.NH_3$ system more of the base and longer time is required in order to obtain maximum carbanion formation. Optimum yields are obtained if the molar ratio of base to substrate to nitrate ester is 2.5:1:3.1. After allowing 10 minutes for anion formation the nitrate ester is added as rapidly as possible while maintaining the temperature below -33°.

The choice of the appropriate base was found to be rather important in certain compounds to obtain high yields of nitro compounds. 4-Methylpyridine was converted to 4-nitromethylpyridine in 66% yield when $NaNH_2$ was used as the base while with KNH_2 the yield was only 21% (eq 17). The sodium salt could be readily



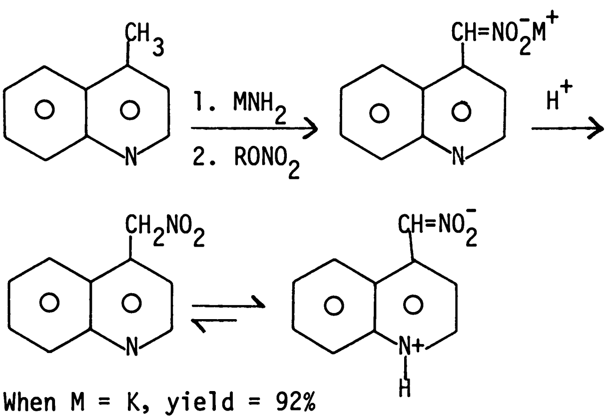
(17)

When M = K, yield = 21%

When M = Na, yield = 66%

purified prior to acidification and was obtained in a yield of 92%. The potassium salt on the other hand was difficult to purify and was highly hygroscopic.

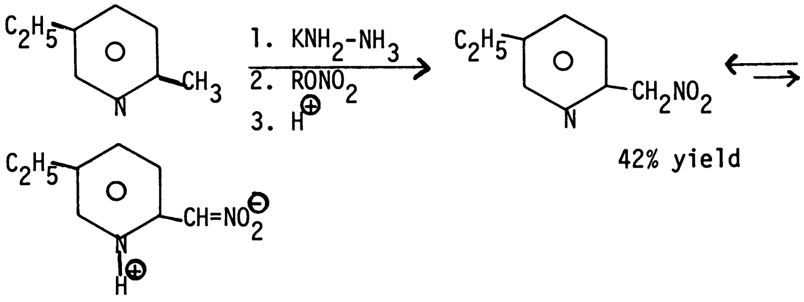
On the other hand, in the case of 4-methylquinoline KNH_2 gave better results than $NaNH_2$ and the yield of 4-nitromethylquinoline was 92% in KNH_2 and 58% in $NaNH_2$ (eq 18).



(18)

When M = K, yield = 92%
When M = Na, yield = 58%

Nitration of 2-methyl-5-ethylpyridine was successful only in KNH_2 and the nitro compound was obtained in 42% yield (eq 19). Apparently $NaNH_2$ is not a strong enough base to form the anion. Only starting material was recovered.

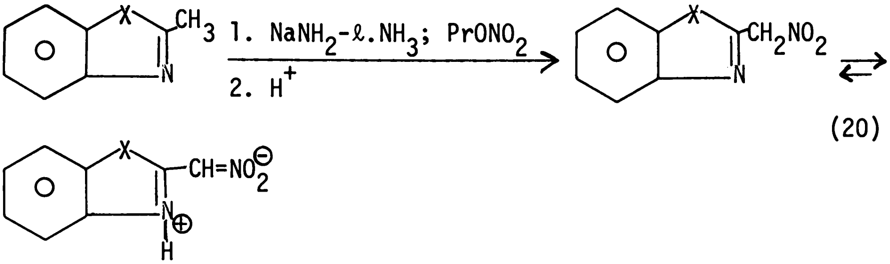


(19)

2-Methylbenzothiazole and 2-methylbenzoxazole were converted to 2-nitromethylbenzothiazole and to 2-nitromethylbenzoxazole in yields of 66% and 62%, respectively (eq 20).

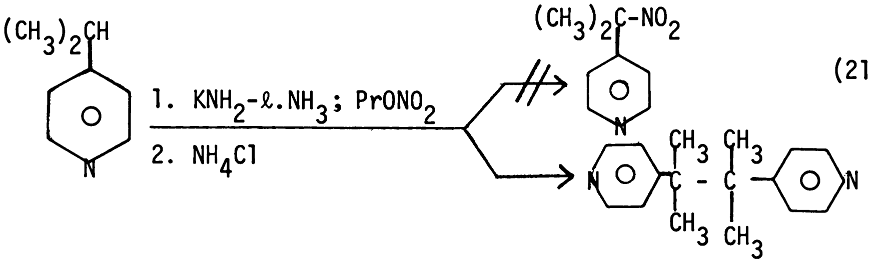
The alkyl nitrate nitration of 4-isopropylpyridine which was expected to give the tertiary nitro compound took an entirely different course. Instead of the nitro compound there was formed the dimer, 2,3-dimethyl-2,3-di(4-pyridyl)butane in a yield of 80% (eq 21). It is very likely that the dimerization reaction proceeds by a radical anion pathway and that the nitro compound

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010



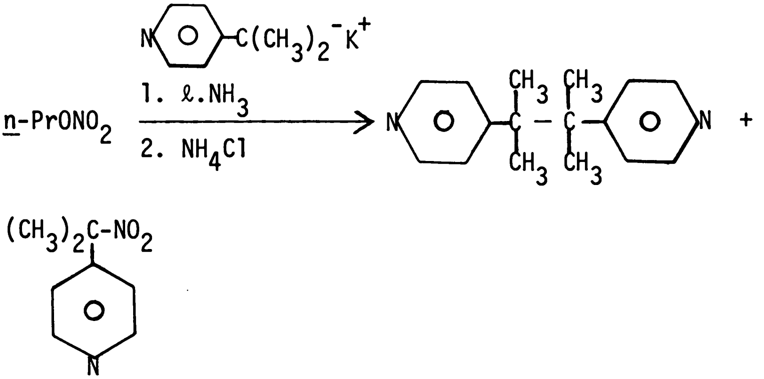
(20)

X = S or O



(21)

is an intermediate in the formation of the dimer (16). In fact both the tertiary nitro compound and the dimer were obtained in yields of 60% and 32% respectively, when, in an inverse addition the anion of 4-isopropylpyridine was generated in liquid ammonia and then was added to a solution of n-propyl nitrate in liquid ammonia at -40° (eq 22).



(22)

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch010

Literature Cited

1. Thiele J., Chem. Ber., (1900) 33, 666; Wislicenus W., ibid. (1900) 33, 771.
2. Wislicenus W. and Endres A., ibid., (1902) 35, 1755.
3. Wieland H., Garbsch P. and Chavin J. J., Justus Liebigs Ann. Chem., (1928) 461, 295.
4. Feuer H., Shepherd J. W. and Savides Ch., J. Amer. Chem. Soc. (1956) 78, 4364.
5. Klager K., J. Org. Chem., (1955) 20, 646.
6. Feuer H. and Savides Ch., J. Amer. Chem. Soc., (1959) 81, 5826.
7. Feuer H. and Vincent, Jr. B. F., J. Org. Chem., (1964) 29, 939.
8. Schaub R. E., Fulmor W. and Weiss M. J., Tetrahedron, (1964) 20, 373.
9. Feuer H., Hall A. M. and Anderson R. S., J. Org. Chem., (1971), 36, 140.
10. Feuer H., Hall A. M., Golden S. and Reitz R. L., J. Org. Chem. (1968) 33, 3622.
11. Feuer H. and Pivawer P. M., J. Org. Chem., (1966) 31, 3152.
12. Feuer H. and Monter R. P., ibid., (1969) 34, 991.
13. Feuer H. and Auerbach M., ibid., (1970) 35, 2551.
14. Feuer H. and Friedman H., ibid., (1975) 40, 187.
15. Feuer H. and Lawrence J. P., ibid., (1972) 37, 3662.
16. Feuer H., Doty J. and Lawrence J. P., ibid., (1973) 38, 417.

11

Heterogeneous Nitration of Benzene

DANIEL F. SCHIEFFERLE,[1] CARL HANSON,[2] and LYLE F. ALBRIGHT

School of Chemical Engineering, Purdue University, West Lafayette, Ind. 47907

[1] Current address: Stauffer Chemical Co., Dobbs Ferry, New York
[2] Current address: University of Bradford, Bradford, England

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Although nitrations of aromatic compounds are of considerable importance, numerous questions are still unanswered concerning both the mechanism of the reaction and the rate limiting step in the two-liquid-phase reaction. The intrinsic chemical kinetics are undoubtedly rate limiting under certain reaction conditions, but diffusion is rate limiting at other reaction conditions.

For the commercial nitrations of several aromatics such as benzene and toluene, the acid phase is a mixture of nitric acid, sulfuric acid, and water. The nitration reactions certainly occur either in the acid phase or at least at the interface between liquid phases. The aromatic reactant must hence be transferred to the interface and possibly also into the acid phase. Thus the design and scale-up of an industrial nitrator is a problem of simultaneous mass transfer and chemical reaction, and it is essential to know which of these is the limiting step in choosing the proper parameters for scaleup.

Albright, Hanson, et al (1,2,3) have reviewed the work of previous investigators and concluded that the criteria sometimes used to determine the rate-limiting step were not adequate. The reaction kinetics measured by some workers (4, 5) exhibit considerable differences even though they claimed to be measuring intrinsic kinetics. Such differences may result from diffusion effects. Recently, Cox and Strachan (6) reported the nitration of chlorobenzene to be kinetically controlled at a nitric acid concentration of 0.032 mole/liter in 70 weight percent sulfuric acid; for the nitration of toluene in the same acid, the rates of chemical reaction and diffusion were of comparable magnitude.

The present investigation was undertaken in order to better define the role of diffusion in the two-phase reaction system at acid concentrations more nearly comparable to those used in industrial practice. Another objective of this work was to obtain quantitative information describing the solubilities of various compounds in each phase.

The specific system studied consisted of a mixed-acid phase of nitric acid, sulfuric acid, and water with benzene as the

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

aromatic reactant. Conditions of temperature and acid concentration were controlled such that only mononitration occurred.

Experimental Details

The continuous-flow stirred-tank reactor (CFSTR) of 50 ml capacity was constructed of stainless steel and was jacketed for temperature control. The reactor was 5.08 cm high and had 3.8 cm inside diameter. Four equally spaced 0.32 cm baffles were welded to the bottom of the reactor. The agitator was a 2.5 cm diameter standard four-blade turbine impeller operated at 3000 rpm.

The aromatic and acid reactants entered the reactor through two 0.32 cm stainless-steel feed lines which protruded into the reactor to a point directly beneath the turbine impeller. The reaction products exited through a 0.16 cm diameter stainless tube located directly opposite the turbine impeller. The product offtake opening of the reactor was connected to a flexible stainless-steel tube; the height of this tube was adjusted so that the reactor was completely filled with liquid-liquid emulsion, as indicated by a sight glass located on top of the reactor. A thermocouple was inserted into the reactor through a stainless-steel tube protruding from the top flange.

The emulsion from the reactor was collected in a glass flask immersed in an ice bath; here it separated by decanting into acid and hydrocarbon phases. The total acidity of the latter phase was measured by titrating a methanolic solution of it with standard sodium hydroxide to a methyl red endpoint. Part of the hydrocarbon phase was water washed, and it was then analyzed by gas chromatography using a Perkin Elmer Model 154 Vapor Fractometer for benzene and nitrobenzene. Certain by-products were also detected when and if they formed.

The acid phase was divided into several portions that were used to make the following measurements. The total acidity (reported as percent sulfuric acid) was determined by titration with a standard sodium hydroxide solution using a methyl purple indicator. Total sulfuric acid was determined in a second sample in a similar manner after the nitric acid and lower oxides of nitrogen were expelled by evaporation on a steam bath. Lower oxides of nitrogen were determined by a redox method. Total nitric acid was determined by difference.

Experimental Results

Extensive results were obtained for the nitration of benzene over a wide range of conditions. In order to help analyze and explain these nitration results, numerous measurements were also made of the equilibrium distribution of reactants and of products between the hydrocarbon and acid phases.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

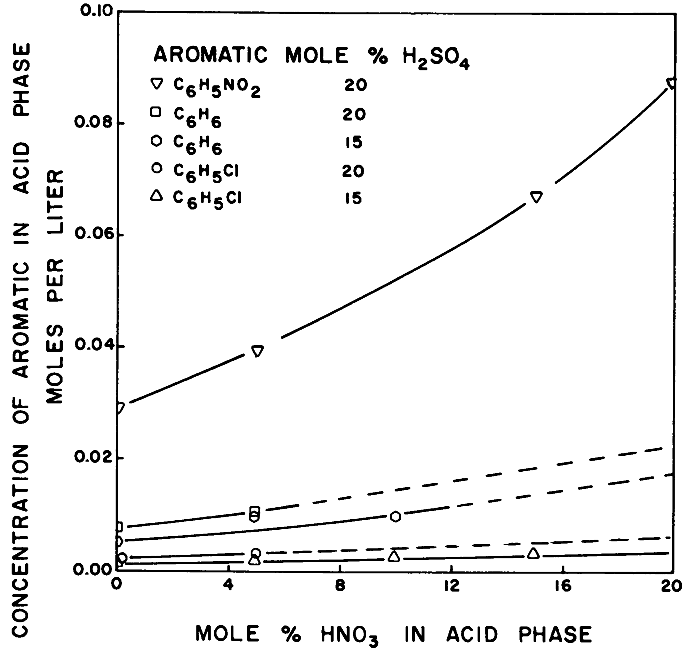


Figure 1. Solubility of aromatic hydrocarbons in several mixed acids at 5°C

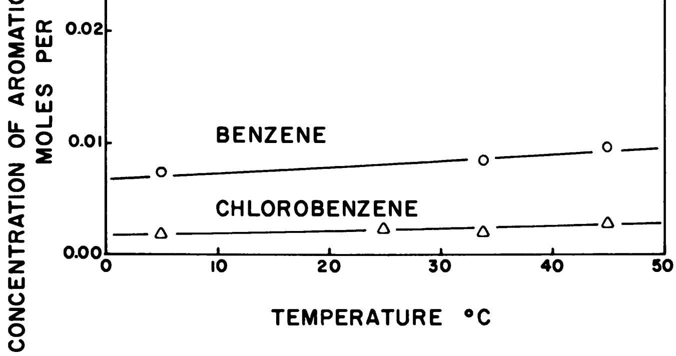


Figure 2. Effect of temperature on solubilities of aromatic hydrocarbons in 20% (mole) sulfuric acid

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Distribution Measurements. The equilibrium distributionsof various aromatics between the two liquid phases were measured experimentally. The acid phase and the organic phase were contacted at the desired temperature and vigorously shaken for several minutes in a separatory funnel. The acid phase was then allowed to separate from the organic phase, and it was then centrifuged to remove all dispersed organic droplets. The dissolved hydrocarbons in the acid phase were extracted with p-xylene, and the extract was analyzed using gas chromatography.

Direct measurements of benzene solubility in mixed acids were not always possible because of the reactivity of the benzene. The following method was used to estimate the distribution of benzene between phases at reaction conditions. First, the distributions of nitrobenzene and chlorobenzene between phases were measured using mixed acids comparable in concentrations to those used in the two-phase reaction study. Nitrobenzene was unreactive in these acids and the amount of chlorobenzene that reacted (while measurements were being made) was negligible in most cases. Second, the distribution of benzene between phases was measured at conditions where reaction did not occur; these measurements were made at low temperatures and/or using mixed acids much less concentrated than those used in the two-phase reaction study. The results of these measurements were then extrapolated to reaction conditions using the data for nitrobenzene and chlorobenzene as a guide.

The concentrations at 5°C of nitrobenzene, benzene, and chlorobenzene in the acid phase are shown in Figure 1 as a function of acid composition. Solubilities of aromatic hydrocarbons in the acid phase increase significantly and almost linearly as the concentration of the nitric acid in the mixed acids increases (and as the concentration of water decreases). Also a small increase of solubility was noted when the concentration of sulfuric acid in the acid phase was increased from 15 to 20 mole percent.

Several measurements with toluene and the results for other aromatics indicated that the relative solubilities of the four aromatic hydrocarbons tested were as follows:

Nitrobenzene > Benzene > Chlorobenzene $\gtrsim$ Toluene

Solubilities of aromatic hydrocarbons in the acid phases increase slightly as the temperature increases. Figure 2 shows the results in 20 mole percent sulfuric acid. Figure 3 indicates the solubility results at 5°C for benzene in mixtures of sulfuric acid and water. A minimum solubility occurs at about 10 to 20 mole percent sulfuric acid, and relatively much higher solubilities occur both in pure water and in more concentrated sulfuric acids.

The distributions of benzene and nitrobenzene between phases are shown in Figure 4 as a function of the organic phase

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

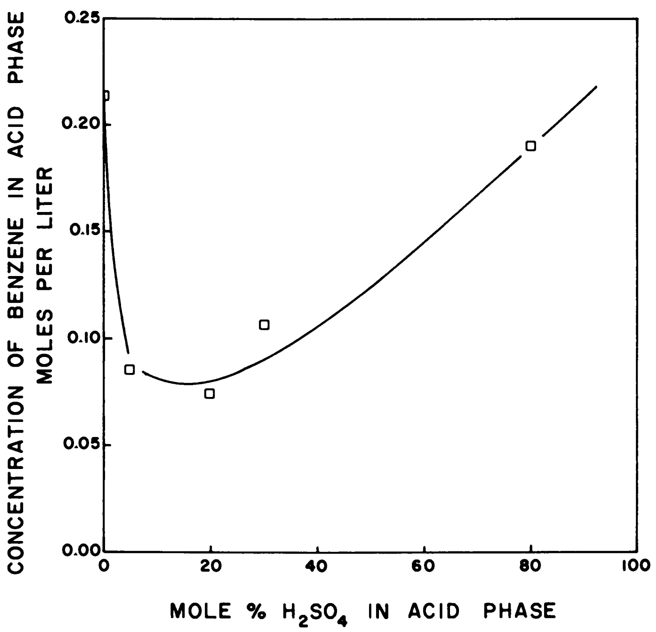


Figure 3. Solubility of benzene in sulfuric acid-water mixtures at 5°C

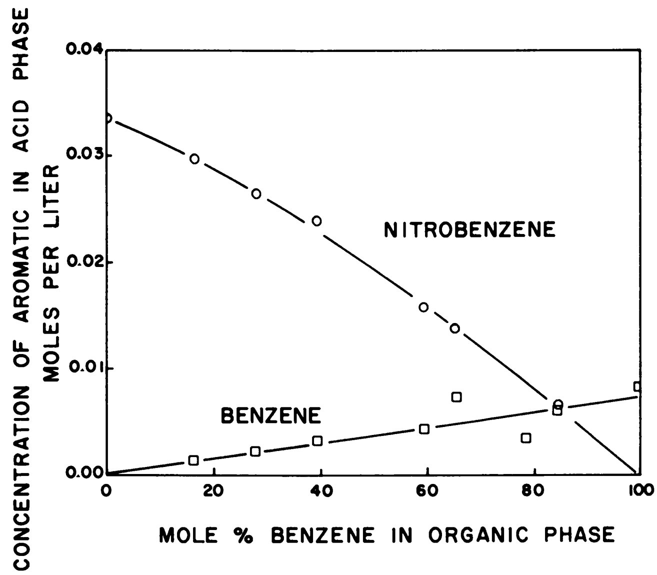


Figure 4. Effect of organic-phase composition on distribution of benzene and nitrobenzene between phases at 33°C (acid phase was 20 mole % sulfuric acid)

composition. These measurements were made at 33°C using an acid phase containing 20 mole percent sulfuric acid and the remainder water. An almost linear relationship occurs between the concentration of aromatic in the acid phase (expressed in moles per liter) and the concentration in the organic phase. Figures 1, 2, and 4 all indicate that nitrobenzene is three or four times more soluble in mixed acids than benzene.

The distributions of nitric acid and sulfuric acid between the two immiscible phases were also measured. When an acid containing 20 mole percent sulfuric acid and the remainder water was equilibrated at 28°C with nitrobenzene, the concentration of sulfuric acid in nitrobenzene was less than 0.1 weight percent. When an acid containing 20 mole percent nitric acid and the remainder water was equilibrated at 26°C with nitrobenzene, the concentration of nitric acid in the nitrobenzene phase was approximately 10 mole percent as shown in Figure 5. In making these measurements, the total acidity of the nitrobenzene phase was measured, and the nitric acid solubility was estimated by difference. It was assumed that the sulfuric acid concentration was in all cases 0.1 percent or less and based on that assumption nitric acid accounted for essentially all of the total acidity of the hydrocarbon phase. The distributions at 26°C of nitric acid between aqueous phases (containing various concentrations of nitric acid and sulfuric acid) and a nitrobenzene phase are also shown on Figure 5.

The distributions of nitric acid between a mixed acid phase (containing 10 percent nitric acid and 20 mole percent sulfuric acid) and an organic phase (containing various mixtures of benzene and nitrobenzene) were measured at 5°C, as shown in Figure 6. Solubility results were also obtained at 26° and 55°C for pure nitrobenzene, and solubility predictions are shown on Figure 6 for mixtures of benzene and nitrobenzene at 26° and 55°C. Solubility of nitric acid increased significantly in the hydrocarbon phase as the nitrobenzene content of this phase increases. Slight increases in nitric acid solubility also occurred with temperature increases in the 5-55°C range.

These measurements clearly indicate that relatively large changes in the distributions of various components between the acid and hydrocarbon phases occur during the course of a batch nitration. Such changes can have important effects on the rate of nitration.

Two-Phase Nitration. Preliminary experiments were performed at 55°C for the purpose of establishing good material balances, estimating the experimental error, and examining the effects of several factors on the two-phase reaction system. Overall material balances within ± 2.5 percent were attained. Balances on individual components were within ± 5.0 percent. Five replicate experiments were included among the preliminary experiments. The standard deviation of the reaction rate was 0.598 and this number

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

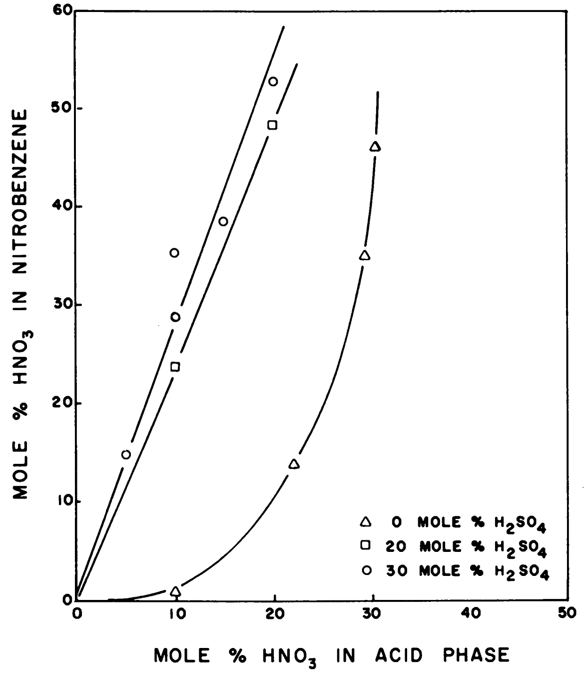


Figure 5. Distribution of nitric acid between a mixed acid phase and a nitrobenzene phase at 26°C

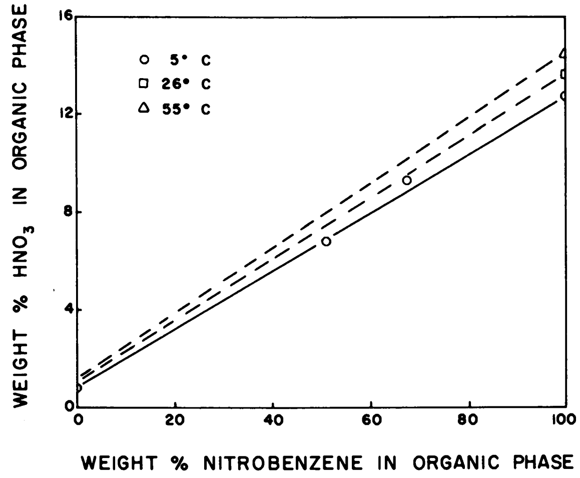


Figure 6. Distribution of nitric acid between benzene-nitrobenzene mixture and mixed acids (10 mole % nitric acid and 20 mole % sulfuric acid)

was 4.6 percent of the mean value.

The rate of nitration was investigated as a function of the composition of the organic phase in a series of runs made at the following conditions: temperature, 55°C; volume fraction of acid phase in two-phase emulsion, 0.67; residence time of emulsion in reactor, 5 minutes; and a product acid that contained approximately 7.5 mole percent nitric acid, 19.5 mole percent sulfuric acid and 73 mole percent water. Figure 7 indicates for these runs that the reaction rate decreased toward zero as the nitrobenzene concentration of the hydrocarbon product stream increased (and there was a consequent decrease in the benzene concentration). There were some experimental difficulties in adjusting the feed acid composition for these runs in order to get exactly the same composition of the product acid. It seems safe to conclude however that the rate of nitration is essentially if not exactly first order relative to the benzene composition in the hydrocarbon phase. (At the high rates of agitation used in the reactor, the compositions of the exit phases can be assumed to be equal to compositions of the two phases in the reactor).

Some organic by-products were apparently formed during nitration. As the nitrobenzene content of the product hydrocarbon stream increased, the color of this stream changed from a light yellow to a dark red-orange. Some of these by-products may be oxidation products. When toluene is nitrated, benzaldehyde is for example sometimes produced (7).

During nitration, part of the nitric acid reacted; most of the acid that reacted produced nitrobenzene but by-products such as nitrous acids were also formed in relatively small amounts. The unreacted nitric acid partitioned itself between the acid and hydrocarbon phases. Figure 8 indicates the fates of the feed nitric acid as a function of composition of the hydrocarbon phase for the runs described above. The fractions of nitric acid that were retained (unreacted) in the product acid and that reacted both decreased as the nitrobenzene content increased toward 100 percent. At the conditions investigated, pure nitrobenzene was essentially unreactive. In these runs, the fraction of feed nitric acid that was extracted by the hydrocarbon phase increased almost linearly from about 2 to 30 percent as the nitrobenzene content increased from 0 to 100 percent. Clearly nitric acid extraction is important at higher benzene conversions (to nitrobenzene).

A series of 20 statistically-designed experiments were made varying five operating variables (at two levels with a half replicate of the statistical design). The variables and levels investigated are as follows:

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

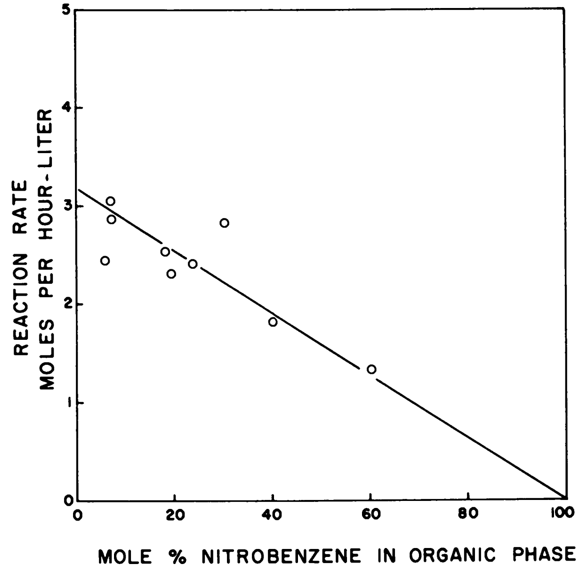


Figure 7. Effect of organic-phase composition on rate of nitration of benzene at 55°C

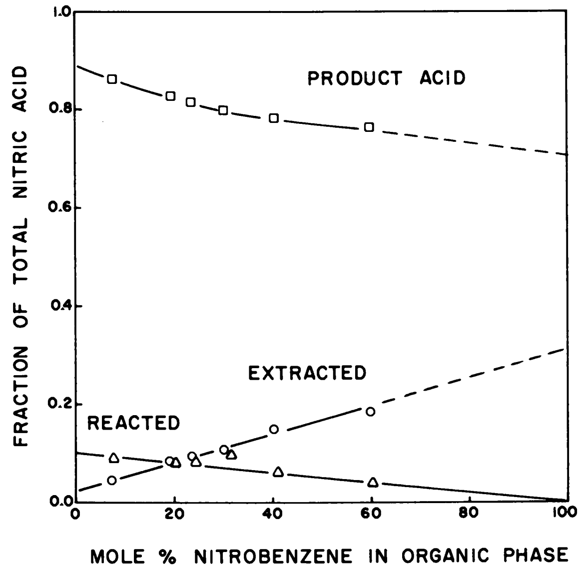


Figure 8. Fate of feed nitric acid during nitration of benzene with mixed acids at 55°C

		low	high
1	Residence time, minutes	3	6
2	Volume fraction of acid phase	0.33	0.60
3	Feed benzene concentration, mole %	60	100
4	Feed nitric acid concentration, mole %	15	25
5	Feed sulfuric acid concentration, mole %	15	20

Nitrotoluene was used as the diluent (at 40 percent concentrations) in those runs in which the hydrocarbon feed contained 60 percent benzene. The nitrotoluene that is unreactive under the conditions investigated was used instead of nitrobenzene in order to permit more accurate measurements of the amounts of nitrobenzene produced, especially when the amounts were small. This technique hence resulted in more accurate measurements of the rates of nitration.

In this series of runs, the product acid compositions varied from 9 to 15 percent nitric acid for a feed acid composition of 15 percent nitric acid and from 11 to 21 percent nitric acid with a feed composition of 25 percent. The benzene concentrations in the organic product varied from 60 to 100 percent when pure benzene was used as the feed hydrocarbon and from 25 to 60 percent when the feed hydrocarbon contained 60 percent benzene. No nitrobenzene was detected in the organic product for three of the 20 runs indicating for these particular runs that the rates of nitration were essentially zero. Measurements of the equilibrium solubility of benzene in the acid phase were almost identical regardless of whether nitrobenzene or nitrotoluene was used as the diluent in the hydrocarbon phase. Four additional (and duplicate) runs were also made to estimate the probable levels of experimental errors. This estimate was pooled with an estimate based on earlier runs.

The correlation model of McKinley and White (5) as developed for toluene nitrations was tested, but failed to correlate the present data. Retesting the model with the data of McKinley and White indicated that differences between predicted and experimental rates of nitration were as great as 120 percent.

The approach originally suggested by Astarita (8) and Dankwerts (9) for gas-liquid systems was modified, and fair success was obtained in correlating the kinetic data of the current investigation. In development of kinetic equations, reaction systems are classified into three categories depending on the relative rates of mass transfer and chemical reaction. The slow reaction regime is characterized by the fact that the amount of the aromatic reactant that reacts in the film at the interface between phases is negligible compared to the amount that diffuses into the acid phase. Either the intrinsic kinetics or the rate of bulk-diffusion of the aromatic reactant may be the rate controlling step. The second type of reaction system is designated as a fast reaction system, and benzene would react in

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

the acid film or at a boundary layer near the interface between the acid and organic phases. Diffusion resistances of benzene in the acid film would be the rate-controlling step. The third category of reaction system is designated as an instantaneous reaction system in which the reaction occurs so quickly that reactants do not coexist in the same region of the liquid. Mathematically, the reaction then occurs at a plane near the interface between the two liquid phases, and the rate of nitration is proportional to the product of the interfacial area and the mass transfer coefficient.

The nitration data of this investigation were first used to discriminate between the kinetic models developed for the slow, fast, and instantaneous reaction systems (or regimes) and second to pick the best kinetic model. In order to do this, values had to be estimated for the concentration of the nitrating species (or entity) in the acid phase, the interfacial concentration of benzene, the kinetic rate constants for acid-phase nitrations, interfacial area (between two liquid phases), and diffusivity values or mass transfer coefficients for benzene. In analyzing the data, the concentration of the nitrating species was assumed to be that of the nitric acid in the acid phase; it is appreciated that this assumption is open to question as will be discussed later but based on available information is probably the best assumption possible. The interfacial concentration of benzene (hC_{ArH}) was estimated based in part on the results obtained in making distribution measurements; h is the distribution coefficient for benzene and C_{ArH} is the benzene concentration in the hydrocarbon phase. Kinetic rate constants (for the second-order nitration reactions occurring in the acid phase) were estimated based on the results of Deno and Stein (10), Coombes et al (11), and Butt (12). They had found that the kinetic rate constant could be correlated in terms of an acidity function. The specific acidity function will be considered in more detail later. Values for the interfacial area and for diffusivity values were estimated employing correlations found in the literature (13,14,15); density and interfacial surface tension values needed to solve these correlations were determined experimentally in this investigation. Schiefferle (16) has reported details of the calculations for determining each of the above-mentioned terms.

Models for the three types of reaction systems as defined by Astarita (8) and Dankwerts (9) were tested for the experimental data using multiple linear regression programs. The best fits of the data were obtained for models that included those terms that would be expected to be important when intrinsic kinetics are rate controlling, i.e. for slow-reaction regimes. Models developed for such a regime have the following general form:

$$R \; \alpha \; H_v^a \, k^b \, C_N^c \, (hC_{ArH})^d \qquad (1)$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

where R = rate of nitration
H_v = volume fraction of acid phase in emulsion
k = kinetic rate constant
C_N = concentration of nitric acid
hC_{ArH} = interfacial concentration of aromatic (benzene in this case)

One of the problems in testing Equation 1 was how to evaluate the kinetic rate constant (k). Earlier investigators (11,12) who had first developed correlations of k versus acidity functions had used mixed acids containing fairly high concentrations of sulfuric acid but low concentrations of nitric acid. They had calculated the acidity function based only on the sulfuric acid content; in their systems, the sulfuric acid accounted for essentially all of the acidity. In the present investigation, however, the mixed acids contained lower concentrations of sulfuric acid and higher concentrations of nitric acid as compared to the earlier investigations. Two techniques were hence tested for measuring acidity functions - one based only on the sulfuric acid concentration and the other based on total acidity. Using the total acidity concept resulted in a better correlation, and a linear regression analysis of Equation 1 yielded the following coefficients:

$$R \quad \alpha \quad H_v^{0.86}\, k^{1.15}\, (hC_{ArH})^{0.60}\, (C_{HNO_3})^{4.45} \tag{2}$$

The value of r^2 for this model was 0.973, although the model showed a significant lack of fit of the data. The calculated F ratio for lack of fit was 36.9 at the probability point 0.05.

When the values of the exponents for the interfacial concentration of benzene and for the volume fraction of the acid phase in the reactor were forced to 1.0, the resulting equation was as follows:

$$R \quad \alpha \quad H_v^{1.0}\, k^{1.19}\, (hC_{C_6H_6})^{1.0}\, C_{HNO_3}{}^{4.31} \tag{3}$$

The value of r^2 for this model was 0.968. The calculated F ratio for lack of fit was 38.9. Equation 3 produced almost as good a correlation as Equation 2.

Discussion of Results

Intrinsic kinetics were probably the rate-controlling step in most if not all of the experimental runs made in this investigation. Reasonably high levels of agitation were provided, and

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

the rates of nitration were relatively low since the acid concentrations were low compared to most commercial nitrations.

Although Equations 2 and 3 do not correlate the rate data as well as desired, the correlations do offer encouragement that the general approach is correct. Theoretical considerations would suggest for reaction conditions in which the intrinsic kinetics were controlling (i.e. mass transfer resistances are not) that the rate would be directly proportional to the volume fraction of the acid in the emulsion, the concentration of benzene in the acid phase, the concentration of the nitrating species, and the reaction rate constant. Failure of the model to show exact first-order dependence of the concentration of benzene in the acid phase is understandable given the approximate nature for estimating the benzene distribution coefficient. Considerable extrapolation of the distribution measurements was necessary in order to estimate the coefficient at reaction conditions. It is encouraging that the model does show nearly first-order dependence on both the volume fraction of the acid in the emulsion and the reaction rate constant.

A main, if not the major, fault with the correlation is that the concentration of the nitrating species was not measured. The species is thought by many investigators to be the nitronium ion (NO_2^+) although these ions have never been directly measured in weak acids such as used in this investigation. It is of interest to note that other investigators(17,18) have also reported high-order dependency for nitric acid similar to the values reported in Equations 2 and 3. Improvement of the present models must await more accurate estimations of the distribution coefficient and a better understanding of the relationship between the concentration of the nitrating species and the composition of the mixed acids used.

Solubility considerations help explain the relative kinetics of benzene and toluene nitrations. Hughes, Ingold, and Hughes (19) found that for competitive nitrations of toluene and benzene in homogeneous systems (where there are no transfer of aromatics between phases) that the kinetic rate constant for toluene was approximately 20 times that for benzene. Yet, in two-phase systems toluene nitrates only about 5 times faster than benzene. In the present investigation, it was found that the solubilities of benzene in acids were about four times greater than either toluene or chlorobenzene. The combination of higher benzene solubilities and of higher k values for toluene exactly explains the difference in relative rates for the two-phase systems assuming that the intrinsic rates are the rate-controlling step.

Distribution measurements such as those made in this investigation are certainly most important in interpreting nitration results. Clearly more solubility information for the aromatic hydrocarbon in the acid phase is needed for the purpose of discrimination between models. The distribution measurements made in this investigation indicate that the solubility of aromatic hydrocarbons in mixed acids varies significantly depending on the compositions of both the acid and hydrocarbon phases and to a lesser extent on temperature. Extraction of significant amounts of nitric acid by nitroaromatics is also of importance, and such extraction may contribute to oxidative side reactions (7).

Literature Cited

1. Albright, Lyle F., Chemical Engineering, April 25, 1966, pp. 169-172.
2. Albright, Lyle F. and Hanson, Carl, Loss Prevention, Vol. 3, CEP Technical Manual (AIChE), (1969), pp. 26-31.
3. Hanson, C., Marsland, J. G., and Wilson, G., Chemistry and Industry, April 23, 1966, pp. 675-683.
4. Barduhn, A. J. and Kobe, K. A., Industrial and Engineering Chemistry, 48, 1305 (1956).
5. McKinley, C., and White, R. R., AIChE Trans., 40, 143 (1944).
6. Cox, P. P., and Strachan, A. N., Chem. Engr. Sci., 26, 1013 (1971).
7. Schiefferle, D. F., "Organic-Phase Aromatic Nitration", M.S. Thesis, Purdue University, West Lafayette, Indiana (1970).
8. Astarita, G., Mass Transfer with Chemical Reaction, Elsevier, Amsterdam, (1967).
9. Dankwerts, P. V., Gas-Liquids Reactions, McGraw-Hill, (1970).
10. Deno, N. C., and Stein, Richard, J. Amer. Chem. Soc., 78, 578 (1956).
11. Coombes, R. G., Moodie, R. B., and Schofield, K., J. Chem. Soc. (B), (1968), pp. 800-804.
12. Butt, K. U., Aromatic Nitration: Comparison of Homogeneous and Heterogeneous Systems, Thesis, Univ. of Bradford (1969).
13. Calderbank, P. H., Trans. Inst. Chem. Engr., 36, 443 (1958).
14. Perkins, L. R., and Geankoplis, C., J. Chem. Engr. Sci., 24, 1035 (1969).
15. Sherwood, T. K., and Reid, R. C., The Properties of Gases and Liquids, McGraw-Hill, (1966).
16. Schiefferle, D. F., "Heterogeneous Nitration of Benzene", PhD Thesis, Purdue University, West Lafayette, Indiana (1972).
17. Bonner, T. G., Hancock, R. A., and Rolle, F. R., Tetrahedron Letters, (1968), pp. 1665-1667.
18. Coombes, R. G., J. Chem. Soc. (B), (1969), pp. 1256-1260.
19. Hughes, E. D., Ingold, C. K., Reed, R. J., and others, J. Chem. Soc., (1950), pp. 2400-2473.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch011

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

12

A Model for Rate of Nitration of Toluene Under Heterogeneous Conditions

J. GILES
ICI Limited, Organics Division, Huddersfield, England
C. HANSON and H. A. M. ISMAIL
Schools of Chemical Engineering, University of Bradford, England

Liquid phase aromatic mononitration under normal industrial conditions is an example of mass transfer with simultaneous chemical reaction. The problem of determining the magnitude and nature of the resistance to interphase transfer has been avoided in much research on nitration kinetics by the simple expedient of working in a solvent with which all reactants are miscible. Early work on the rate of the two liquid phase heterogeneous process has been reviewed by Albright and Hanson(1-4). They pointed out that, contrary to the assumption commonly made previously, all mass transfer resistance has not necessarily been eliminated if the reaction rate becomes constant at high levels of agitation.

Subsequently, Hanson and co-workers(5,6) studied the heterogeneous mononitration of both toluene and chlorobenzene in a miniature CFSTR (45ml capacity) using nitrating acid typical of that employed in industry (15 mole % HNO_3, 30 mole % H_2SO_4, 55 mole % H_2O). The results were shown to be inconsistent with a simple kinetic model and it was concluded that diffusional resistances play a more important part in determining nitration rates in the two liquid phase region than had hitherto been supposed. This is in agreement with the extensive results, also for small scale reactors, published during the last few years by Strachan and co-workers(7-11), who have demonstrated that the overall rate can be correlated by a simple kinetic model at low sulphuric acid concentrations but that diffusional resistances become important at higher sulphuric acid concentrations. This is consistent with the effect of sulphuric acid on the kinetics of homogeneous nitration reactions. The sulphuric acid is seen as an ionizing medium for nitric acid to nitronium ions (assumed the true nitrating agent) and so the availability of the latter increases with sulphuric acid concentration.

Any attempt to interpret observed heterogeneous nitration rates in terms of mass transfer with simultaneous chemical reaction demands a knowledge of the interfacial area available. The CFSTR in which the original work was performed was too small

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

to allow for insertion of photographic probes and so it was decided to build a larger reactor which would also allow the effect of scale to be investigated. A one stage CFSTR was chosen in preference to alternative forms of reactor in the hope of gaining results which would be comparable with those from typical industrial nitrators. A photographic method was adopted for measurement of drop size and hence interfacial area. It was chosen in preference to alternatives such as light transmittance because of the large hold-up of dispersed organic phase necessitated by the stoichiometry of the reaction. It had the additional advantages of being independent of the physical properties of the system (which change with degree of conversion) not influenced by color (colored by-products are formed), and of giving the drop size distribution rather than just a mean value. The results of the drop size studies have been reported elsewhere (12). Provision was made for measurement of power input in addition to agitation speed to give more information applicable to scale-up.

Experimental

Reactor. The reactor, which was 2.5 litre in capacity, was designed as closely as possible to the Standard Tank Configuration(13) and was constructed in EN58J stainless steel. It is shown in Figure 1. Cooling was provided by means of a coil supported in the tank baffles. Two sets of probes were fitted near the tank wall: one set opposite the impeller and the other midway between the impeller and the top of the reactor. A microscope camera was fitted onto one probe of each pair, while a high speed flash was inserted in the other. The camera probe was built from a microscope and incorporated a graticule. After calibration, the latter was used to measure drop sizes. By measuring at least 300 drops, a maximum error of 3% was involved in determination of the Sauter mean drop diameter.

The agitator (a six blade flat-blade turbine) was driven by a 1 HP, 800rpm direct current electric motor, the speed of which was controlled by a thyristor drive unit. The power input was measured mechanically. The motor was supported vertically by two bearings attached to the drive shaft in such a way that the motor casing was free to rotate. To prevent rotation of the casing, an arm was attached which acted on a load cell at a known distance from the shaft. The torque was registered directly on a meter. A bearing was provided in the base of the reactor. There was a liquid seal in the lid through which the effluent was discharged, so avoiding any possible vortex.

The reactor was fitted with an iron-constantan thermocouple housed in a stainless steel sheath. A small amount of oil was maintained in the latter to ensure good thermal contact. The thermocouple was wired to a temperature compensated recorder and

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

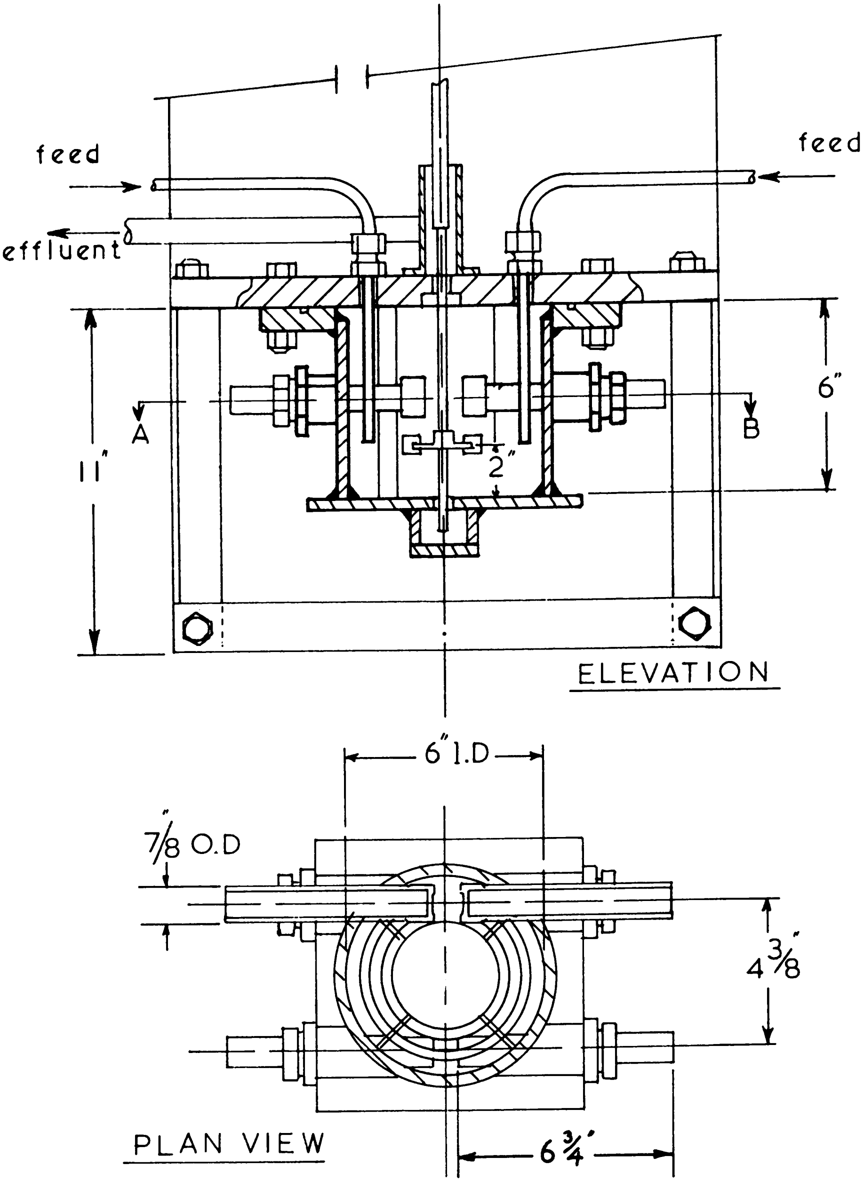


Figure 1. Reactor dimensions

provided measurement to ± 0.25°C. The temperature of the reactor contents was controlled by varying the flow of water to the cooling coil.

The reactants were stored in glass aspirators and were fed to the reactor by means of metering pumps. The capacities of the latter gave a range of residence times in the reactor from 6 to 60 minutes. The flow rates were checked before and after each run.

Further details of the equipment are available elsewhere(14).

Materials. Because of the large quantities required, the reagents had to be purchased in commercial quantities. The best commercially available grades were employed. The toluene was industrial nitration grade. GLC analysis showed it to contain 0.21 wt.% paraffins but no detectable benzene or xylenes. The acids analysed as follows:

	Density (gm/cc at 30°C)	Normality
Sulphuric Acid	1.827	35.10
Nitric Acid	1.362	12.88

Nitrating acid was prepared by mixing the constituents in a stainless steel bucket submerged in a water bath, the temperature being maintained below 20°C to reduce the possibility of forming nitrosylsulphuric acid.

Procedure. The reactor was initially filled with water. The agitator was switched on at the required speed. The reactants were then introduced at the appropriate rate using the metering pumps. The cooling water flow was adjusted to keep the temperature constant. When steady state was reached (usually after about five residence times), the power input was noted, the dispersion photographed and samples of the product taken. The latter were drawn through a sampling tube connected to the main effluent pipe near the exit from the reactor. The tube was purged to remove any material from the previous run. Three separate samples were taken during each run: (i) the organic phase washed with water, (ii) the acidic organic phase, and (iii) the aqueous phase. The former was obtained by running the sample into water and then separating the two phases. The organic phase was given a second water wash. Samples of the unwashed phases were obtained by running some of the reaction products into a separating funnel and allowing the phases to separate. This took place quite rapidly so the extent of reaction during the sampling would be small. Samples of the separated phases were removed quickly from areas well away from the interface.

Depending on the degree of conversion, either or both the product phases were found to be colored, indicating the presence of by-products. The color disappears if the product is

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

collected in water and so it has not been noticed by many previous workers since it is normal to quench the reaction by running the sample into an excess of water. However, the coloration is commonly observed in industry and causes an effluent problem when the organic product is washed to effect its removal. Because of the obvious complexity of the process and the industrial importance of the by-product formation, a fairly comprehensive analysis of the products was undertaken in the hope of throwing further light on the problem.

Analysis

The organic product phase was analysed for toluene, the various mononitrotoluene isomers, nitric, nitrous and sulphuric acids. The aqueous phase was anlysed for nitric and nitrous acids, total acidity and mononitrotoluene.

The presence of sulphuric acid in the organic phase was checked by the standard barium chloride method but none could be detected. Since the total acidity of the organic phase could be accounted for by the nitric and nitrous acids found, the sulphuric content was assumed negligible.

The organic phase was also analysed for water by the Carl-Fischer technique but none was found. This was confirmed by infra-red analysis of the organic phase, where no water absorption peaks were found.

The toluene and mononitrotoluene isomer concentrations in the organic phase were obtained by GLC analysis using a Pye 104 Gas-Liquid Chromatograph fitted with a Kent Chromalog integrator. A 12ft column packed with Apiezon L on Chromasorb P of 60-80 mesh was employed and gave good separation working at a temperature of 163°C. N-tetradecane was used as internal standard. Regular checks on performance were made using a sample of known composition. Analytical accuracy was within ± 1%.

Nitric acid in the aqueous phase was determined by the method used by Barduhn and Kobe(15), i.e. titration against standard ferrous sulphate. Nitrous acid was analysed using formation of a diazonium salt between m-nitroaniline and nitrous acid. Standard m-nitroaniline solution was titrated against a known volume of the sample acidified with dilute hydrochloric acid until testing with starch iodide paper demonstrated the absence of free nitrous acid. The total acidity of the aqueous phase was obtained by titration against standard sodium hydroxide.

In the case of the organic phase, the nitrous acid content was found by first extracting into an excess of water and then using the above method on the aqueous extract. To obtain the total acidity of the organic phase, a known volume was washed with water and the mixture made alkaline. After shaking for five minutes to ensure extraction of all the acid from the

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

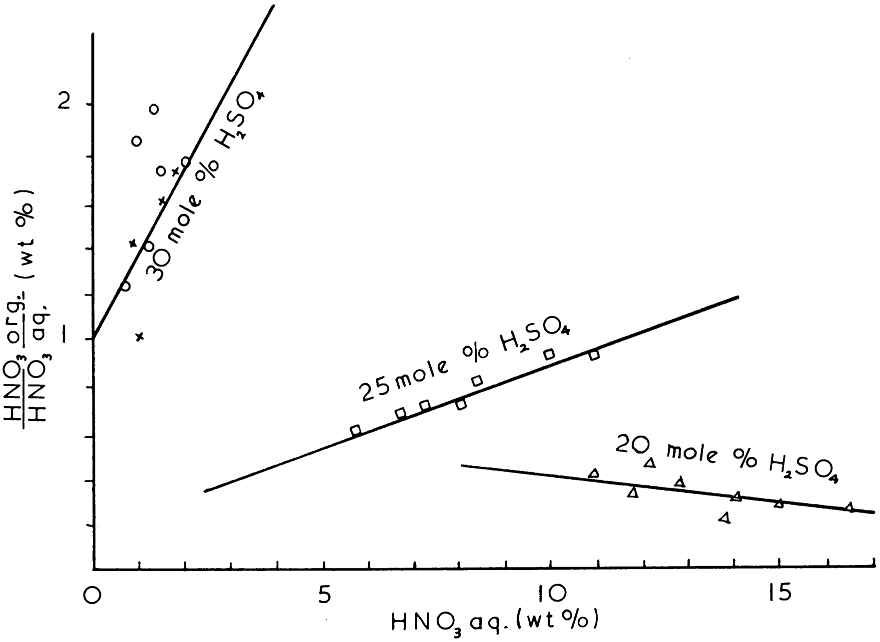


Figure 2. Distribution of nitric acid between aqueous and organic phases at 30°C

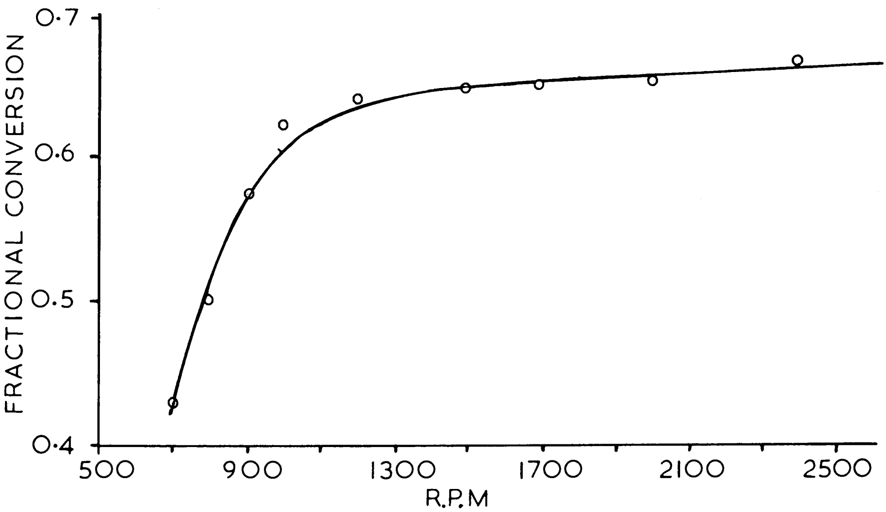


Figure 3. Effect of agitator speed on fractional conversion

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

organic phase, the excess alkali in the aqueous layer was determined by titration with standard hydrochloric acid. The total acidity was assumed due to nitric and nitrous acids only. Reproducible results (i.e. ± 2%) could only be obtained when the organic phase samples were stored at low temperature. At ambient temperature the acidity was observed to decrease slowly.

The mononitrotoluene concentration in the acid phase was determined by ultra-violet spectroscopy.

With all the above analyses, it was found possible to obtain good overall mass balances (within ± 4%).

Results and Discussion

Phase Compositions. It was found that considerable quantities of nitrous acid are formed during the nitration reaction and it was possible to correlate this with production of by-products. This question is discussed in detail elsewhere(14).

The comprehensive analysis undertaken showed that considerable quantities of nitric acid are extracted into the organic phase and are thus temporarily "lost" to the reaction. At high conversions, the concentration in the organic phase was comparable with that in the aqueous. As might be expected, the amount extracted was found to increase with aqueous phase acidity. The results are illustrated in Figure 2.

Effect of Agitation. The effect of agitation was studied for an acid mixture with a composition typical of that used for industrial mononitrations (15 mole % HNO_3, 30 mole % H_2SO_4) and an acid to toluene volumetric feed ratio of 1.5:1. The maximum possible fractional conversion under these conditions is 0.775. With a residence time of 10 minutes and a temperature of 30°C, the fractional conversion varied with agitation, as shown in Figure 3. The plot against power consumption shown in Figure 4 demonstrates a sharp division into two regions. That in which conversion rises rapidly with agitation has often been assumed to involve substantial mass transfer resistances, increase in agitation reducing these by increasing the interfacial area. However, it is also possible that the hold-up of dispersed phase changes with agitation in this region. Since reaction takes place predominantly in the aqueous phase, any change in the phase ratio within the reactor for a given overall flow rate will cause a change in the space time of the aqueous phase and hence in the conversion. This was found, as illustrated in Figure 5. It will be seen from this that the junction between the two regions in Figures 3 and 4 coincides with attainment of a steady hold-up in Figure 5.

In the second region, conversion is relatively insensitive to agitation and it has often been claimed that this indicates the elimination of mass transfer resistances. However, it will be seen that conversion does continue to increase, even though

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

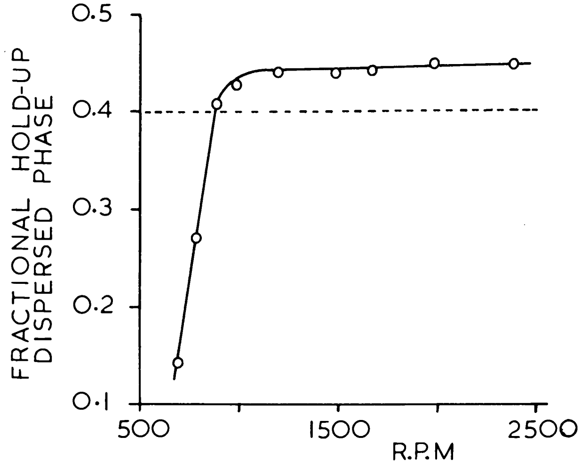


Figure 4. Effect of power input on fractional conversion

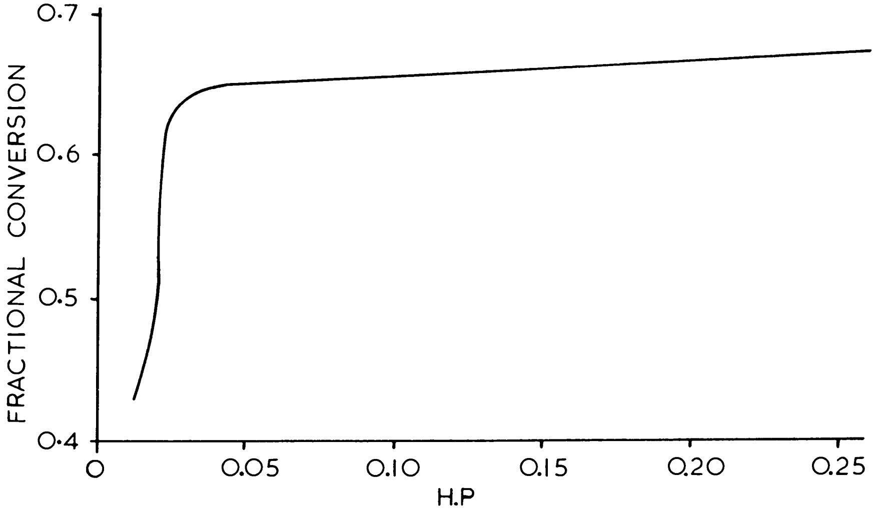


Figure 5. Hold-up of dispersed phase as function of agitation

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

slowly, throughout this region. The insensitivity to agitation is hardly surprising. Firstly, the mean drop size shows little change. Then from the point of view of mass transfer coefficient in the dispersed phase, drop interaction will be largely suppressed and the drops behave as rigid spheres, while fully turbulent conditions exist in the continuous phase. Thus little change would be expected in the coefficient.

The overall shape of the curve in Figure 3 can therefore be easily explained in terms of mixing and mass transfer phenomena and does not indicate the elimination of diffusional resistances at high degrees of agitation. This is the same conclusion as was drawn from the small scale work.

Effect of Space Time. One of the authors(5) has previously used space time as a test for a simple kinetic model. Operating a small scale CFSTR with a fixed feed ratio, a fixed agitation rate (in excess of the critical value for full turbulence) and a constant temperature, space time was varied by adjustment of the flow rate. The results were analysed on the assumption that the following kinetic rate equation applied:

$$R = k' C_{N_A} C_{T_O} \qquad \ldots(1)$$

The constant k' includes the distribution coefficient for toluene between the two phases, the assumption being that reaction takes place homogeneously throughout the aqueous phase. The value of k' was found to vary with space time and this was taken as evidence for mass transfer control.

In the above work the concentration of nitric acid was found from analysis of the quenched product emulsion, it being tacitly assumed that all the acid would be present in the aqueous phase. During the present work, as was shown earlier, appreciable quantities of nitric acid were found in the organic phase. This extraction of nitric acid effectively reduces the amount available for reaction (C_{N_A} in equation 1) and so decreases the rate of reaction. This was appreciated by McKinley and White(16) and by Barduhn and Kobe(15).

The data in the present work, allowing for extraction of nitric acid into the organic phase, were used in equation 1 to calculate values of the apparent rate constant k'. These are shown in Figure 6 and demonstrate a marked trend. It can only be concluded from this that either (a) equation 1 is not the true rate equation, (b) the distribution coefficient for toluene changes appreciably with conversion, or (c) the measured rate includes a contribution from mass transfer.

Effect of Phase Ratio. As with the smaller scale reactor (5), a series of experiments was carried out in which the

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

residence time of the total emulsion was kept constant but the phase ratio varied (agitator speed and temperature maintained constant). The work was mainly carried out with feed acids containing 20 and 25 mole % H_2SO_4. Once again, it was not found possible to correlate the results by a simple kinetic model.

Effect of Phase Inversion. A convenient criterion for the existence of a mass transfer resistance which has not been widely used in the past is the effect of phase inversion. This leads to changes in both interfacial area per unit volume and mass transfer coefficients. However, residence time is not affected and so phase inversion should have no effect on the rate of a kinetically controlled process. Two runs were carried out at 30°C with an agitator speed of 1700rpm, a residence time for the dispersion of 25 mins., a feed phase ratio of 1.0 and the standard nitrating acid with 30 mole % H_2SO_4. By varying the start-up procedure, it was possible to disperse either phase. With the aqueous phase dispersed, the fractional conversion of the toluene was 0.473. With the organic phase dispersed it was found to be 0.502. The measured hold-up of organic phase in the reactor was the same in each case. With the aqueous phase dispersed the Sauter mean drop diameter was 205µ, whereas with the organic dispersed it was 125µ. The difference in the degree of conversion provides conclusive proof for the presence of a mass transfer resistance and the need for a rate model which will take this into account. It is also abundantly clear that the failure to eliminate the mass transfer resistance in the early work using a miniature CFSTR was not a function of scale and that the effect is likely to be of importance in industrial reactors, certainly with nitrating acid containing 30 mole % H_2SO_4.

Theory

The general state of knowledge of mass transfer with simultaneous chemical reaction has been ably summarized by Danckwerts(17). Hanson and co-workers(18) have more recently discussed theories for liquid-liquid systems with particular reference to solvent extraction.

As explained above, experimental data with nitrating acids of compositions typical of those employed industrially cannot be reconciled with theoretical models assuming a uniform rate of reaction through either or both phases. Such models will only apply to slow reactions. The other extreme is an instantaneous reaction, which would lead to reaction taking place at a reaction plane. This cannot be applicable to mononitrations since nitric acid is always found in the organic phase. Development of a model to describe the overall rate demands a knowledge of the locale of the reaction. Conflicting opinions have been expressed

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

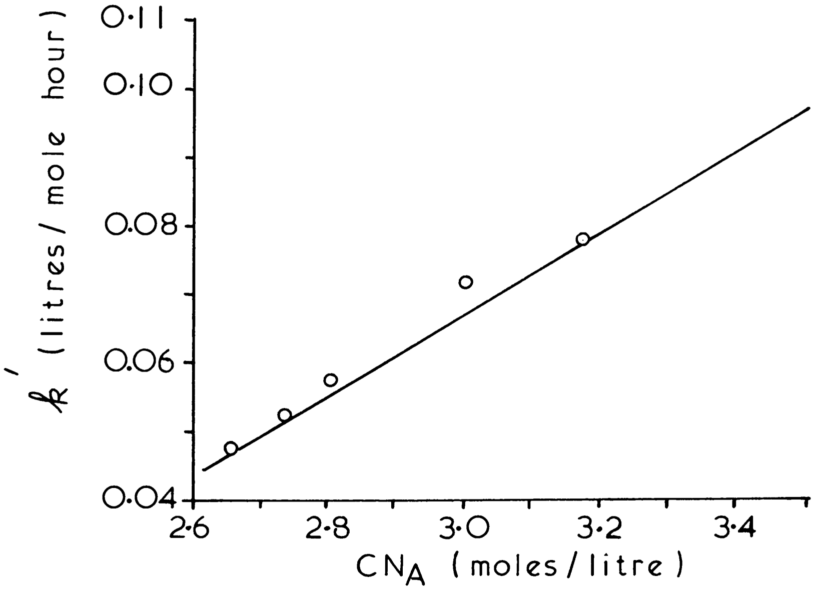


Figure 6. Variation of apparent reaction velocity constant with nitric acid concentration in aqueous phase

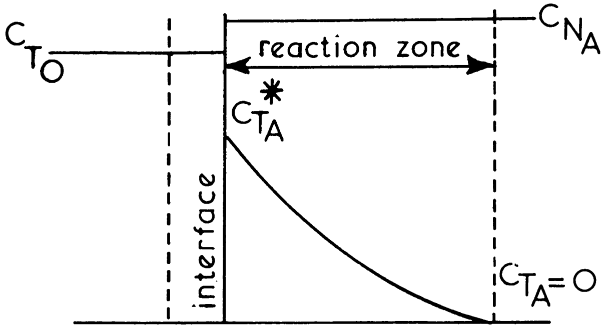


Figure 7. Interfacial concentration profiles assumed in model

in the literature as to whether any reaction takes place in the organic phase. Lewis and Suen(19), having been able to separate the two phases rapidly and follow the disappearance of HNO_3 from the organic layer, concluded that some reaction does take place in the organic phase. Barduhn and Kobe(15), however, showed that while the HNO_3 disappears from the organic layer, there is no corresponding disappearance of toluene. More recently, Sohrabi(20) has studied reaction in the organic phase and demonstrated that the maximum rate of reaction is many orders of magnitude less than that in the aqueous phase. Thus, while some reaction may take place in the organic phase during heterogeneous nitration, its contribution to the overall rate will be extremely small (<0.001%) and can be justifiably neglected.

In view of the above, the most realistic model to consider for aromatic mononitrations under these conditions appears to be of a fast reaction taking place in a zone in the aqueous phase adjacent to the interface. The aromatic will diffuse through this zone while reacting. This is illustrated in Figure 7. The mathematical approach for this situation has been developed by Astarita(21) and Danckwerts(17).

The following steps are envisaged, considering toluene as the hydrocarbon:

(1) Toluene diffuses through the organic phase towards the interface,
(2) From the interface the toluene diffuses into the bulk aqueous phase,
(3) While diffusing into the aqueous phase the toluene reacts to form mononitrotoluene,
(4) The nitrotoluene formed diffuses back through the aqueous phase to the interface,
(5) From the interface the nitrotoluene diffuses into the bulk organic phase,
(6) Nitric acid diffuses from the bulk aqueous phase towards the interface, reacting with the toluene en route,
(7) The water formed diffuses back into the bulk aqueous phase,
(8) Some nitric acid diffuses from the interface into the bulk organic phase.

For the reasons discussed above, processes (2) and (3) are probably rate determining. To simplify derivation of a model, the following assumptions can be made:

(1) Reaction in the organic phase is negligible,
(2) The nitronium ion, NO_2^+, mechanism is applicable,
(3) The water concentration is essentially constant throughout the aqueous phase,
(4) The nitric acid and NO_2^+ concentrations are constant throughout the aqueous phase,
(5) There is a simple distribution relationship between the concentration of toluene in the organic phase (assumed

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

uniform) and the interfacial concentration of toluene in the aqueous phase, i.e. $C_{T_O} = \phi C^*_{T_A}$.

By a material balance over a film of thickness dx in the reaction zone:

$$D \frac{\partial^2 C}{\partial x^2} = r(C) \qquad \text{...(2)}$$

The following boundary conditions are applicable:

At the interface: $C = C^*_{T_A}$ when $x = 0$

In the bulk aqueous phase: $\frac{dC}{dx} = 0$ when $C = C_{T_A} = 0$

Solution of the differential equation gives the rate of reaction per unit volume of reacting mixture:

$$R = A.\sqrt{2D\int_0^{C^*_{T_A}} r(C).dC} \qquad \text{...(3)}$$

Assuming the overall reaction may be represented as:

$$ArH + HNO_3 \rightarrow ArNO_2 + H_2O$$

the rate of reaction is:

$$r(C) = kC_{T_A}C_{N_A} \qquad \text{...(4)}$$

Substitution gives:

$$R = A\sqrt{DkC_{N_A}}.C^*_{T_A}$$

$$= \frac{A}{\phi}\sqrt{DkC_{N_A}}.C_{T_O} \qquad \text{...(5)}$$

Testing of Model

For nitrating acid of constant sulphuric acid concentration, it could be thought that $\frac{1}{\phi}\sqrt{Dk}$ might remain constant. However, when the rate data obtained were inserted in equation 5, it was found that $\frac{1}{\phi}\sqrt{Dk}$ varied linearly with nitric acid concentration, giving a straight line for each sulphuric acid concentration and temperature. Typical results are shown in Figure 8. This is not sufficient to condemn the model since the supposition that $\frac{1}{\phi}\sqrt{Dk}$ might remain constant is clearly extremely simplistic. There is no reason to suspect the constancy of the homogeneous rate constant k but the values of ϕ and D are quite likely to vary with composition of the acid phase.

A strong indication that the model predicts the correct form of rate dependence was obtained from the effect of temperature on rate for a fixed acid composition. Temperature coefficient has been used by earlier workers as a test for kinetic control in the heterogeneous system but the limitations of this approach have been emphasised by Albright and Hanson(1-4). If equation 1 is applied to the present rate data for 25 mole % H_2SO_4 it shows $k'_{50°C}/k'_{30°C} = 3.3$. Using the activation energy for homogeneous nitration of toluene in the aqueous phase measured by Butt(22) (19.5 K.cal./mole) in the Arrhenius equation predicts $k_{50°C}/K_{30°C} = 7.1$. The difference provides further proof that the k' values are not true reaction velocity constants since the change in distribution coefficient of toluene (incorporated in k') with temperature could not explain the difference. However, the ratio of the values of $\frac{1}{\phi}\sqrt{Dk}$ for 50°C and 30°C with 25 mole % H_2SO_4 calculated via the model from the measured rate data is 2.75. If it is assumed that the values of ϕ and D do not change appreciably over this temperature range, this would predict $\sqrt{k_{50°C}}/\sqrt{k_{30°C}} = 2.75$ or $k_{50°C}/k_{30°C} = 7.6$, in good agreement with the value of 7.1 from homogeneous data, remembering that ϕ and D will vary to some extent with temperature.

Further testing of the model clearly demanded a knowledge of the values of ϕ and D under the conditions of the nitration experiments. The distribution coefficients of toluene between organic phases with varying concentrations of mononitrotoluene and aqueous phases of different compositions have been measured (23). These show ϕ to be a function of both toluene conversion and nitric acid concentration for a fixed sulphuric acid concentration. Values of the molecular diffusion coefficient for toluene as a function of the acid phase composition have also been measured using a laminar-jet technique(24). These show some dependence on composition but not to a great extent.

This leaves the second order rate coefficient for toluene nitration in aqueous solution (k) as the only missing parameter. The most reliable data are probably those of Coombes et al(25). Unfortunately, they used nitric acid concentrations much below those found in heterogeneous nitrations and there is some uncertainty as to how they should best be extrapolated. Thus Cox and Strachan(9) have attributed deviations in their results to the probability of k values in their nitrating mixtures being higher than those measured by Coombes et al. Schiefferle(26) found it necessary to modify the acidity function concept to account for the contribution of the nitric acid dissociation to the proton concentration and suggested that k should be related to the total acidity rather than just the sulphuric acid concentration. A model based on this concept gave a better fit to his experimental results.

For the present work, estimation of k was based on a different approach. Sulphuric acid concentrations were calculated on a "nitric acid free" basis. This simply implies correction of the sulphuric acid concentration in the nitrating

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

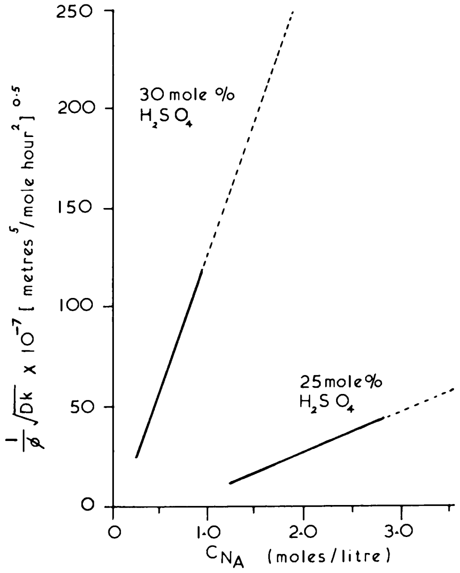


Figure 8. Variation of $1/\phi\sqrt{Dk}$ as Function of nitric acid concentration in aqueous phase

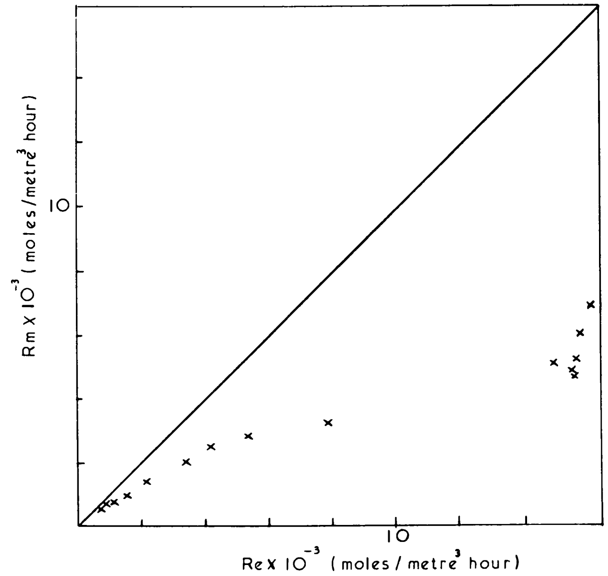


Figure 9. Comparison between predicted and experimental nitration rates for stirred tank reactor

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

acid as if nitric acid is present in extremely small concentration, thus making the use of Coombes' data more reasonable. The latter were obtained at 25°C, while the temperature adopted in the present work was 30°C, and so they had to be corrected to 30°C using the Arrhenius equation.

Values of $\frac{1}{\phi}\sqrt{Dk}$ were calculated from the above data and hence nitration rates predicted for the conditions covered in the experimental work. The results are compared in Figure 9 with the rates actually measured in the CFSTR. There is clearly no agreement. One obvious explanation is that the model may not be applicable. Before dismissing the model, however, other possible causes of the discrepancy should be considered. The most questionable parameter used in predicting the rate is the diffusion coefficient. This was measured in a laminar-jet and so corresponds to molecular diffusion. In all runs in the CFSTR, except those to test the effect of phase inversion, the aqueous phase was continuous and fully turbulent conditions were established. Thus, while the conditions in the dispersed phase might have corresponded to molecular diffusion, the predominant mass transfer process in the continuous aqueous phase would certainly be eddy diffusion. This would give an actual rate greater than that predicted, which is what is found in Figure 9.

To test whether the cause of the deviation between the predicted nitration rate and that found in the CFSTR lay in the turbulence created in the latter, experiments were carried out in which toluene was actually nitrated in the laminar-jet apparatus. This should ensure applicability of the measured molecular diffusion coefficients. Some problems were experienced since the very short contact time in the laminar-jet resulted in low conversions and consequent difficulty in achieving high analytical accuracy. In this case, however, predicted and measured rates agreed to within 10%, as will be seen from Figure 10. Further details of this work are available elsewhere(24). In view of the experimental difficulties involved, this degree of agreement appears to validate the model and prove its applicability to toluene mononitration, certainly with nitrating acid containing 30 mole % H_2SO_4.

If it is accepted that the model is applicable to aromatic nitration under these conditions, then experimental rate data from a CFSTR can be used to calculate the effective diffusion coefficient in the CFSTR.

Scale-Up

A subsidiary objective of the main work described in this paper was to obtain an insight into scale-up criteria for continuous nitrators of the CFSTR type operating under conditions comparable with this study. One obvious design parameter is that the vessel should operate above the critical agitator speed necessary to give fully turbulent conditions and a constant dispersed phase hold-up. However, from the data obtained there would not appear to be any advantage in operating appreciably above the critical value, particularly as a higher degree of agitation represents a higher power input (power input increases as the cube of the agitator speed). The problem therefore becomes one of predicting the critical agitator speed in reactors of different size. In this work it was found that the critical speed approximates to the start of the turbulent region on the power curve, a plot of power number against Reynolds number as used by Rushton and co-workers(27). This is illustrated in Figure 11 and is of the classic form showing a fall to a minimum in the transition region followed by a constant value of power number through the turbulent region.

Whatever scale-up approach is adopted, it is essential that both vessels should be completely similar geometrically.

Scale-up at constant Reynolds number (proportional to ND^2) has often been used in an attempt to obtain hydrodynamic similarity. However, the total power consumption in the turbulent region is proportional to N^3D^5. Therefore, if the Reynolds number is kept constant but the physical dimensions of the vessel doubled, the total power input will be halved. This gives the same overall flow pattern but not equality of instantaneous velocities and seems of improbable validity. Scale-up using constant impeller tip speed ($= \pi DN$) ensures that the velocities leaving the impellers are the same in each case and has found fairly wide acceptance. Constant tip speed means that power input per unit volune ($\propto N^3D^2$) falls as scale is increased but the total power input increases, which is more reasonable.

Scale-up at constant power input per unit volume has been criticised for homogeneous sytems as leading to excessive power inputs in the scaled-up vessel. However, it was found in this work that the interfacial area per unit volume is proportional to N^3D^2. Hence, in view of the proportionality of nitration rate to interfacial area shown in this work, scale-up on the basis of constant power input per unit volume appears the most logical approach when designing for nitrating acids containing sulphuric acid concentrations such that the fast reaction diffusion controlled mechanism applies, e.g. as with the 30 mole% H_2SO_4 mixture typically employed for industrial mononitrations.

Conclusions

The rate of nitration of toluene by nitrating acid of composition 15 mole % HNO_3, 30 mole % H_2SO_4, 55 mole % H_2O, which is typical of that used in industry for mononitration, is not controlled entirely by the chemical kinetics of the process but mass transfer between the phases also plays an important role. It has been shown that the rate can be modelled in terms of a

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

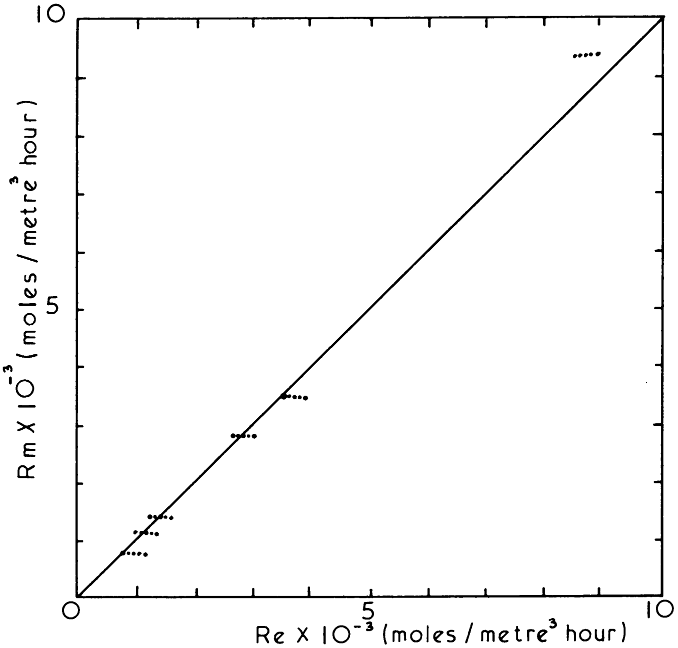


Figure 10. Comparison between predicted and experimental nitration rates in laminar jet

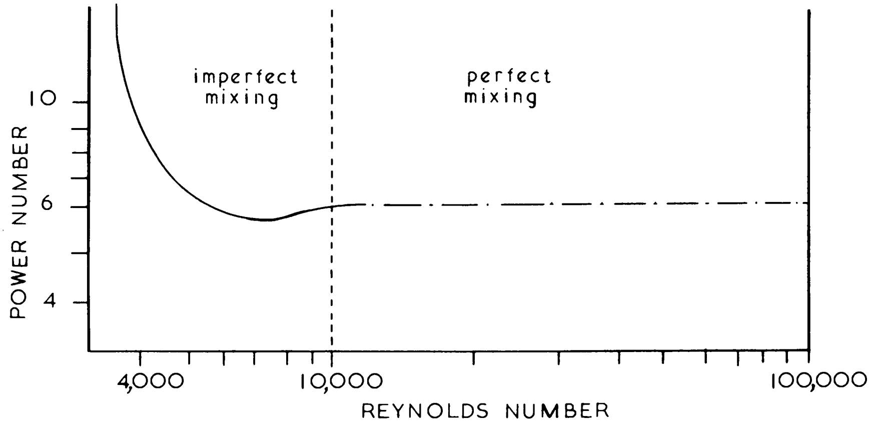


Figure 11. Typical plot of Power number as function of Reynolds number

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

fast reaction taking place in a zone in the aqueous phase adjacent to the interface. Application of the model demands a knowledge of the diffusivity of the aromatic substrate in the aqueous phase under the hydrodynamic conditions found in the reactor and so it is not possible to predict rates for all types of nitrator.

Acknowledgements

The authors would like to express their appreciation for financial support for this work from Messrs Hickson & Welch Ltd., Castleford, UK.

Notation

A	Interfacial area per unit volume
C	Concentration
D	Diffusion coefficient for toluene in aqueous phase
N	Agitator speed
R	Rate of reaction per unit volume
k	Reaction velocity constant
k'	Apparent or pseudo reaction velocity constant
x	Distance from interface
ϕ	Distribution coefficient for toluene (= C_{T_O}/C_{T_A})

Subscripts

A	Acid phase
N	Nitric acid
O	Organic phase
T	Toluene

Superscript

*	Interfacial

Literature Cited

1. Hanson,C.,Marsland,J.G. and Wilson,G.: Chemy.Ind.,(1966) 675.
2. Albright,L.F.: Chem.Engng.,(1966) 73 (9), 169.
3. Albright,L.F.: in Kirk-Othmer "Encyclopaedia of Chemical Technology" 2nd Ed.,(1967) 13, 784.
4. Albright,L.F. and Hanson,C.: Chem.Engng.Prog.Tech.Manual "Loss Prevention", (1969) 3, 26.
5. Hanson,C.,Marsland,J.G. and Wilson,G.: Chem.Engng.Sci., (1971) 26, 1513.
6. Hanson,C.,Marsland,J.G. and Naz,M.A.: Chem.Engng.Sci.,(1974) 29, 297.
7. Cox.P.R. and Strachan,A.N.: Chem.Engng.Sci.,(1971) 26, 1013.

8. Cox,P.R. and Strachan,A.N.: Chem.Engng.Sci.,(1972) 27, 457.
9. Cox,P.R. and Strachan,A.N.: Chem.Engng.Jl.,(1972) 4, 253.
10. Chapman,J.W.,Cox,P.R. and Strachan,A.N.: Chem.Engng.Sci., (1974) 29, 1247.
11. Cox,P.R. and Strachan,A.N.: Proceedings International Solvent Extraction Conference 1974 (Society of Chemical Industry, London) Vol.3, p.2415.
12. Giles.J.W.,Hanson,C. and Marsland,J.G.: Proceedings International Solvent Extraction Conference 1971 (Society of Chemical Industry, London) Vol.1, p.94.
13. Holland,F.A. and Chapman,F.S.: "Liquid Mixing and Processing", Reinhold (1966).
14. Giles,J.W.: PhD Thesis, University of Bradford, UK (1970).
15. Barduhn,A.J. and Kobe,K.A.: Ind.Engng.Chem.,(1956) 48, 1305.
16. McKinley,C. and White,R.R.: Trans.AIChE.,(1944) 40, 143.
17. Danckwerts,P.V.: "Gas-Liquid Reactions", McGraw-Hill (1970).
18. Hanson,C.,Hughes,M.A. and Marsland,J.G.: Proceedings International Solvent Extraction Conference 1974 (Society of Chemical Industry, London) Vol.3, p.2401.
19. Lewis,W.K. and Suen,T.J.: Ind.Engng.Chem.,(1940) 32, 1095.
20. Sohrabi,M.: PhD Thesis, University of Bradford, UK (1972).
21. Astarita,G.: "Mass Transfer with Chemical Reaction", Elsevier (1967).
22. Butt,K.U.: MSc Thesis, University of Bradford, UK (1969).
23. Hanson,C. and Ismail,H.A.M.: Paper accepted for publication in J.Appl.Chem.Biotechnol.
24. Ismail,H.A.M.: PhD Thesis, University of Bradford (1973).
25. Coombes,R.G.,Moodie,R.B. and Schofield,K.: J.Chem.Soc.(B), (1968) 800.
26. Schiefferle,D.: PhD Thesis, Purdue University, USA (1972).
27. Rushton,J.H.,Costich,E.W. and Everett,H.J.: Chem.Eng.Prog., (1950) 46, 395 and 467.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch012

13

Two Phase Nitration of Toluene in Constant Flow Stirred Tank Reactors

ALEC N. STRACHAN

Department of Chemistry, Loughborough University of Technology,
Loughborough, Leicestershire, England

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

A number of studies (1-5) have been made of the nitration of toluene in CFSTRs (constant flow stirred tank reactors). A comparison of the reactor volumes and conditions employed is shown in Table I.

Table I. CFSTR studies of toluene nitration

Authors	Reactor volume /cm^3	Stirring speed in most runs /rpm	Principal strengths of H_2SO_4 employed /mole %	[HNO_3] in acid phase measured
McKinley and White 1944 (1)	635	1,520	20,25,30,32.5	Yes
Brennecke and Kobe 1956 (2)	1.3	10,000	25,30,35	No
Barduhn and Kobe 1956 (3)	2,000	1,900	30.7,34,37	Yes
Hanson, Marsland and Wilson 1971 (4)	40	6,000	30	No
Hanson, Marsland and Giles 1971 (5)	2,500	1,500	20,25,30	Yes

McKinley and White (1) found that plots of $\log(R_a/X_T)$ versus log N were linear for different sulphuric acid strengths as shown in Figure 1. R_a is the moles of toluene nitrated per liter of the acid phase per hour, X_T the mole fraction of toluene in the organic phase and N the mole % nitric acid in the acid phase. The data of Barduhn and Kobe (3) covering considerably higher reaction rates were correlated in the same manner as shown in Figure 2. Unfortunately neither Brennecke and Kobe (2) nor

Hanson, Marsland and Wilson (4) measured the acid phase concentration of nitric acid in the reactor, and without this information no meaningful quantitative correlation and interpretation of their results is possible. Lastly, Hanson, Marsland and Giles (5), in the most recent study, obtained very similar results and trends to those of McKinley and White (1).

The early workers (1,3) claimed the rates they measured were kinetically controlled, but the evidence in support of their claims was critically examined by later workers (6,7) and found wanting. Albright and Hanson (7) went so far as to conclude in 1969 that toluene nitration in the two phase is mass transfer controlled under all conditions so far investigated. Recent results (8,9) with a batch reactor must cast doubts upon this conclusion. This paper therefore seeks to clarify the conditions under which kinetic and mass transfer control occur in the nitration of toluene in CFSTRs and to provide an explanation for the rate correlations shown in Figures 1 and 2.

Three Regimes

Most workers (3,7,10) are agreed that in the two phase system the nitration reaction with toluene occurs almost exclusively in the acid phase. Batch reactor studies (8,9) show that at low acid strengths the rate is kinetically controlled and given by $R_a = k_2[HNO_3][T]_a$, where k_2 is the rate constant for homogeneous nitration in the acid phase, and $[HNO_3]$ and $[T]_a$ are the acid phase concentrations of nitric acid and toluene respectively.

Over a short range of intermediate acid strengths a slow reaction diffusional regime occurs in which the rate $R_a = a'k[T]_a$, a' being the interfacial area per unit volume of the acid phase and k the overall mass transfer coefficient. Finally at high acid strengths a fast reaction regime is observed where $R_a = a'\sqrt{Dk_2[HNO_3]}[T]_a$, D being the diffusivity of toluene in the acid phase.

Value of $[T]_a$

Within a CFSTR the organic phase is principally a mixture of toluene and nitrotoluenes. Such a mixture is unlikely to deviate greatly from ideal behaviour. Hence $[T]_a$ to a good approximation is equal to $X_T[T]_a^s$, where X_T is the mole fraction of toluene in the organic phase and $[T]_a^s$ is the saturation concentration of toluene in the acid phase when the organic phase is pure toluene.

Change from Kinetic to Mass Transfer Control

The slow reaction diffusional regime marks the transition from kinetic to mass transfer control. Thus the change is to be expected when $R_a = a'k[T]_a = a'kX_T[T]_a^s$, or when $R_a/X_T \simeq a'k[T]_a^s$.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

The measurement of a' in a CFSTR is not easy and has only been achieved by Hanson, Marsland and Giles (5). They found a' to be between 300 and 600 cm^2/cm^3. The value of k is probably between 1 and 3 × 10^{-3} cm/s (11,12) and that of $[T]^s_a$ at 35°C around 3 × 10^{-3} mol/dm^3 (13). Thus $a'k[T]^s_a$ is likely to be *ca* 3 × 10^{-3} mol dm^{-3} s^{-1} or 10 mol dm^{-3} $hour^{-1}$. When R_a/X_T is less than this, kinetic control is likely to operate, whereas when it is greater, mass transfer control is to be expected. In the majority of McKinley and White's runs, R_a/X_T is less than 10 mol dm^{-3} $hour^{-1}$ (Figure 1), whereas in all of Barduhn and Kobe's it is greater (Figure 2).

Kinetic Regime

In the kinetic regime $R_a = k_2[HNO_3][T]_a = k_2[HNO_3]X_T[T]^s_a$, or $R_a/X_T = k_2[HNO_3][T]^s_a$. For low concentrations of nitric acid $[HNO_3] = FN$ where F is a constant and given by 1000d/(98S + 18(100-S)), d and S being the g/cm^3 density and mole % strength of the sulphuric acid respectively. Hence for low N, $R_a/X_T = k_2[T]^s_aFN$ and plots of $\log(R_a/X_T)$ versus log N will be linear with slopes of +1.

Values of $k_2[T]^s_aF$

The results shown in Figures 1 and 2 were obtained at 35°C. Values of k_2 and $[T]^s_a$ at 25°C can be interpolated from published data (14,13) and these are listed in Table II. The activation energy E_2 = 16.1 kcal mol^{-1} in 70 wt % (30 mole %) sulphuric acid (8) and from the behaviour of other aromatics (14,15) is likely to decrease by 670 cal mol^{-1} for each 1 wt % increase in sulphuric acid strength. Values of E_2 estimated in this way and those of k_2 at 35°C calculated by their use are also given in Table II.

In several different strengths of sulphuric acid toluene is found to be *ca* 1.2 times more soluble at 35°C than at 25°C corresponding to a heat of solution of 3,350 cal mol^{-1} (8,13). The solubilities at 35°C shown in Table II were calculated from those at 25°C using this factor. The Table also lists the values of F calculated from standard information (16) and the results of multiplying the 35°C values of k_2, $[T]^s_a$ and F together. From these the variations of R_a/X_T with N at 35°C, to be expected if the rate is kinetically controlled, are obtained and are shown as broken lines in Figures 1 and 2.

McKinley and White's Data

It is clear from Figure 1 that for 30 mole % H_2SO_4 the agreement between the experimental and predicted variation of R_a/X_T with N assuming kinetic control is excellent. For 25 mole % H_2SO_4 there is also reasonable agreement between the observed and predicted values of R_a/X_T at the lowest experimental values

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

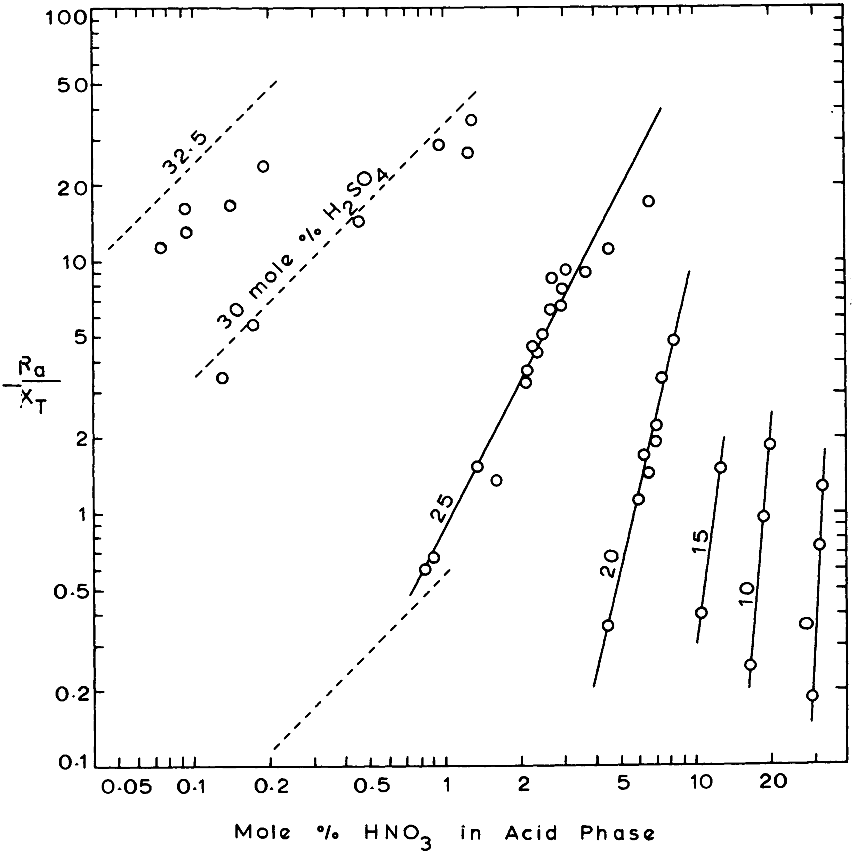


Figure 1. The data of McKinley and White (1)

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

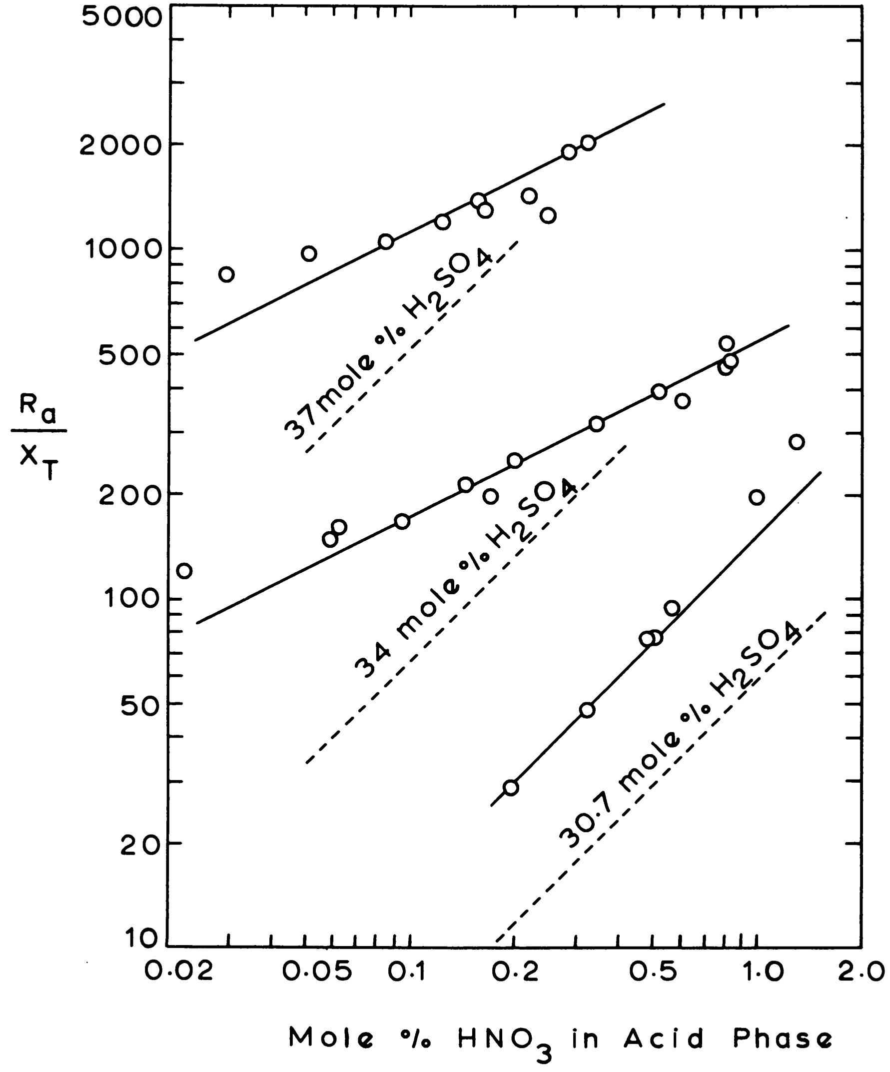


Figure 2. The data of Barduhn and Kobe (3)

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

Table II. Values of various quantities at different sulphuric acid strengths

H_2SO_4 strength /mole %	k_2 25°C /dm^3 mol^{-1} s^{-1}	E_2 /kcal mol^{-1}	k_2 35°C /dm^3 mol^{-1} s^{-1}	$[T]_a^s$ 25°C /mol dm^{-3}	$[T]_a^s$ 35°C /mol dm^{-3}	F /mol dm^{-3}	$k_2[T]_a^sF$ 35°C /mol dm^{-3} $hour^{-1}$
25	$5{\cdot}28 \times 10^{-2}$	19·9	$1{\cdot}57 \times 10^{-1}$	$2{\cdot}05 \times 10^{-3}$	$2{\cdot}46 \times 10^{-3}$	0·407	$5{\cdot}66 \times 10^{-1}$
30	3·80	16·2	9·23	$2{\cdot}20 \times 10^{-3}$	$2{\cdot}64 \times 10^{-3}$	0·384	$3{\cdot}37 \times 10$
32·5	$2{\cdot}63 \times 10$	14·6	$5{\cdot}85 \times 10$	$2{\cdot}50 \times 10^{-3}$	$3{\cdot}00 \times 10^{-3}$	0·373	$2{\cdot}36 \times 10^{2}$
30·7	6·55	15·8	$1{\cdot}56 \times 10$	$2{\cdot}29 \times 10^{-3}$	$2{\cdot}75 \times 10^{-3}$	0·380	$5{\cdot}87 \times 10$
34	$7{\cdot}55 \times 10$	13·6	$1{\cdot}59 \times 10^{2}$	$2{\cdot}67 \times 10^{-3}$	$3{\cdot}20 \times 10^{-3}$	0·366	$6{\cdot}70 \times 10^{2}$
37	$6{\cdot}03 \times 10^{2}$	11·5	$1{\cdot}13 \times 10^{3}$	$2{\cdot}99 \times 10^{-3}$	$3{\cdot}59 \times 10^{-3}$	0·354	$5{\cdot}17 \times 10^{3}$

of N. In the runs at strengths of sulphuric acid of 25 mole % and below, N is no longer small. This is the principal reason why the $\log(R_a/X_T)$ versus log N plots for these strengths have slopes greater than +1. The rate constant k increases with acidity. At low N the acidity is determined solely by the sulphuric acid acid and if the strength of this is constant, so is k_2. But when N is appreciable, the nitric acid itself contributes to, and increases, the total acidity, and hence increases k_2. Thus $R_a/X_T = k_2[T]_a^s FN$ becomes proportional to a power of N greater than +1.

This complication however does not detract from the general conclusion that in most of McKinley and White's runs at strengths of sulphuric acid of 30 mole % and below the rate of nitration is kinetically controlled.

Finally Figure 1 shows that with 32.5 mole % H_2SO_4 the experimental values of R_a/X_T all fall below those predicted if kinetic control were still operating. They are also all above the 10 mol dm^{-3} $hour^{-1}$ mark. Both factors point to the rate of nitration in these runs being mass transfer controlled. It is also possible that the runs at highest N with 25 and 20 mole % H_2SO_4 where R_a/X_T is greater than 10 are also mass transfer controlled, the fall off in the rate due to the onset of mass transfer control being compensated by an increase in k_2 due to the high values of N.

Fast Reaction Regime

In the fast reaction regime $R_a = a'\sqrt{Dk_2[HNO_3]}[T]_a = a'\sqrt{Dk_2[HNO_3]}X_T[T]_a^s$. Hence $R_a/X_T = a'D^{\frac{1}{2}}k_2^{\frac{1}{2}}[T]_a^s[HNO_3]^{\frac{1}{2}}$ which for low nitric acid concentrations $= a'D^{\frac{1}{2}}k_2^{\frac{1}{2}}[T]_a^s F^{\frac{1}{2}}N^{\frac{1}{2}}$. Plots of $\log(R_a/X_T)$ versus log N will therefore be linear with slopes of $+\frac{1}{2}$. To go further and calculate the exact values of R_a/X_T requires a precise knowledge of a' which is unfortunately not available for either McKinley and White's or Barduhn and Kobe's runs.

Barduhn and Kobe's Data

It can be seen from Figure 2 that Barduhn and Kobe's data can be correlated by lines of slope +1 for 30.7 mole % H_2SO_4 and lines of slope $+\frac{1}{2}$ for 34 and 37 mole % H_2SO_4. This points to kinetic control with 30.7 mole % H_2SO_4 and mass transfer (fast reaction) control with 34 and 37 mole % H_2SO_4. Thus there is good agreement between Barduhn and Kobe's and McKinley and White's data as to where the transition from kinetic to mass transfer control occurs.

However at all three acid strengths the experimental R_a/X_T are in each case higher than those predicted assuming kinetic control, whereas they would be expected to be either equal or lower. This is a puzzling anomaly. It could be due to a syste-

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

matic error in the values of R_a/X_T or N in Barduhn and Kobe's data, but only further investigation can decide whether or not this is the correct explanation.

The Data of Other Workers

In all Brennecke and Kobe's (2) and Hanson, Marsland and Wilson's runs (4), R_a/X_T is greater than 10 mol dm^{-3} $hour^{-1}$ and this is also true of Giles, Hanson and Marsland's runs (5) with 30 and 25 mole % H_2SO_4. Hence in these runs it is highly likely that the nitration rates are mass transfer controlled. Values of R_a/X_T lower than 10 mol dm^{-3} $hour^{-1}$ were observed by Giles, Hanson and Marsland (5) in runs with 20 mole % H_2SO_4 and in these kinetic control is almost certainly operating.

Implications for Industrial Reactors

The mononitration of toluene is often carried out industrially using 30 mole % H_2SO_4. If two CFSTRs are used in series the rate may be mass transfer controlled in the first where N is appreciable and kinetically controlled in the second where N is low.

Implications for Other Aromatics

For any aromatic A the transition from kinetic to mass transfer control will occur when $R_a/X_A \simeq a'k[A]_a^s$, X_A being the mole fraction of A in the organic phase and $[A]_a^s$ the solubility of A in the acid phase. The value of a'k is unlikely to vary widely from one aromatic to another. Hence the probability of encountering kinetic or mass transfer control depends largely on the solubility of the aromatic in the acid phase. The more soluble the aromatic, the more likely is its nitration rate to be kinetically controlled. Thus, since nitroaromatics are much more soluble in sulphuric acid than their parent compounds, it is highly probable that the rates of industrial di- and tri-nitration in CFSTRs are kinetically controlled.

Summary

The rate of nitration of toluene in a CFSTR is kinetically controlled when low acid strengths are used and R_a/X_T is below 10 mol dm^{-3} $hour^{-1}$. It is mass transfer controlled when high acid strengths are employed and R_a/X_T is above 10 mol dm^{-3} $hour^{-1}$.

Notation

$[A]_a^s$	solubility of aromatic in the acid phase, mol dm^{-3}
a'	interfacial area per unit volume of the acid phase, cm^{-1}
D	diffusivity of toluene in the acid phase, cm^2 s^{-1}

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

d	density, g cm^{-3}
E_2	activation energy for homogeneous nitration, kcal mol^{-1}
F	$[HNO_3]/N$, mol dm^{-3}
$[HNO_3]$	concentration of nitric acid in the acid phase, mol dm^{-3}
k	overall mass transfer coefficient, cm s^{-1}
k_2	second order homogeneous nitration rate constant, dm^3 mol^{-1} s^{-1}
N	mole % nitric acid in the acid phase
R_a	rate of nitration per volume of acid phase, mol dm^{-3} $hour^{-1}$
S	mole % sulphuric acid
$[T]_a$	concentration of toluene in the acid phase, mol dm^{-3}
$[T]_a^s$	solubility of toluene in the acid phase, mol dm^{-3}
X_A	mole fraction of aromatic in the organic phase
X_T	mole fraction of toluene in the organic phase

Literature Cited

1. McKinley C. and White R.R., Trans.A.I.Ch.E. (1944) 40, 143.
2. Brennecke H.M. and Kobe K.A., Ind. Engng Chem. (1956) 48, 1298.
3. Barduhn A.J. and Kobe K.A., Ind. Engng Chem. (1956) 48, 1305.
4. Hanson C., Marsland J.G. and Wilson G., Chem. Engng Sci. (1971) 26, 1513.
5. Giles J.W., Hanson, C. and Marsland J.G., Proc. Int. Solv. Extr. Conf. (1971), 94, Society of Chemical Industry, London; Giles J.W., Ph.D. Thesis, University of Bradford (1970).
6. Hanson C., Marsland J.G. and Wilson G., Chemy Ind. (1966) 675.
7. Albright L.F. and Hanson C., Chem. Engng Prog. Tech. Manual "Loss Prevention" (1969) 3, 26.
8. Cox P.R. and Strachan A.N., Chem. Engng Sci. (1972) 27, 457.
9. Cox P.R. and Strachan A.N., Chem. Engng J. (1972) 4, 253.
10. Sohrabi M., Ph.D. Thesis, University of Bradford (1972).
11. Chapman J.W., Cox P.R. and Strachan A.N., Chem. Engng Sci. (1974) 29, 1247.
12. Cox P.R. and Strachan A.N., Proc. Int. Solv. Extr. Conf. (1974), 2415, Society of Chemical Industry, London.
13. Cerfontain H. and Telder A., Rec. Trav. Chim. Pays-Bas (1965) 84, 545.
14. Coombes R.G., Moodie R.B. and Schofield K., J. Chem. Soc. (B), (1968), 800.
15. Coombes R.G., Crout D.H.G., Hoggett J.G., Moodie R.B. and Schofield K., J. Chem. Soc. (B), (1970), 347.
16. Fasullo O., "Sulphuric Acid", McGraw-Hill, New York (1965).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch013

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch014

14

Two Phase Nitration of Chlorobenzene in 79.8% Sulphuric Acid

JOHN W. CHAPMAN and ALEC N. STRACHAN

Department of Chemistry, Loughborough University of Technology,
Loughborough, Leicestershire, England

It has been previously shown (1) that with 70.2 wt % sulphuric acid and low concentrations of nitric acid the two phase nitration of chlorobenzene in a stirred batch reactor is kinetically controlled. This is because under these conditions $k_2[HNO_3]$ is very much less than a'k, k_2 being the second order rate constant for homogeneous nitration in the acid phase, $[HNO_3]$ the acid phase concentration of nitric acid, a' the interfacial area per unit volume of the acid phase and k the overall mass transfer coefficient. As the sulphuric acid strength is raised, the value of k_2 increases rapidly (2). Before long $k_2[HNO_3]$ becomes greater than a'k and transition from kinetic to mass transfer control occurs (3).

The present investigation was undertaken with the object of obtaining data with which to check theoretical predictions concerning the nitration rate under mass transfer controlled conditions. A stirred cell was employed since this has the advantage of a known and fixed value of a' and one which is much smaller than that for a stirred reactor (3), thus making even more certain that rates are mass transfer controlled.

Experimental

Two Phase Nitration. The stirred cell and the materials and procedure employed were the same as described previously (3), except that the stirring speed was reduced from 65 to 50 rpm to achieve a smoother interface. A constant acid phase composition of 0.56 mol dm^{-3} nitric acid in 79.8% sulphuric acid was used throughout.

Homogeneous Nitration. Values of k_2 were determined by means of a Nortech SF-3A stopped-flow spectrometer. Equal volumes of dilute solutions of chlorobenzene and nitric acid in 79.45% sulphuric acid were mixed in a thermostat controlled to ± 0.001°C, and the change in the transmittance at 350 nm with time recorded on a storage oscilloscope. The concentrations of

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

chlorobenzene and nitric acid after mixing were 0.98 × 10^{-3} and 1.88 × 10^{-2} mol dm^{-3} respectively. Good pseudo first order behaviour was observed in all cases and since the nitric acid was in excess, k_2 values were obtained by equating the pseudo first order constants with $k_2[HNO_3]$.

Solubility Determinations. The solubilities of chlorobenzene, $[CB]_a^s$, in 79.55% sulphuric acid were determined by the same method as that employed with 70.2% acid (1).

Results

The Table shows the variation with temperature of R_a, the moles of chlorobenzene nitrated per liter of the acid phase per second, and of k_2 and $[CB]_a^s$, each at a sulphuric acid strength close to 80%.

Table. Value of R_a, k_2 and $[CB]_a^s$ at various temperatures

Temperature /°C	R_a 79.8% H_2SO_4 /mol dm^{-3} s^{-1}	k_2 79.45% H_2SO_4 /dm^3 mol^{-1} s^{-1}	$[CB]_a^s$ 79.55% H_2SO_4 /mol dm^{-3}
10	1.82 × 10^{-6}		2.20 × 10^{-3}
15		129	2.29 × 10^{-3}
20			2.98 × 10^{-3}
25	4.43 × 10^{-6}	256	3.18 × 10^{-3}
30			3.15 × 10^{-3}
35	8.14 × 10^{-6}	454	3.73 × 10^{-3}
45	1.37 × 10^{-5}	936	3.91 × 10^{-3}
54.5	2.17 × 10^{-5}		
55		1220	

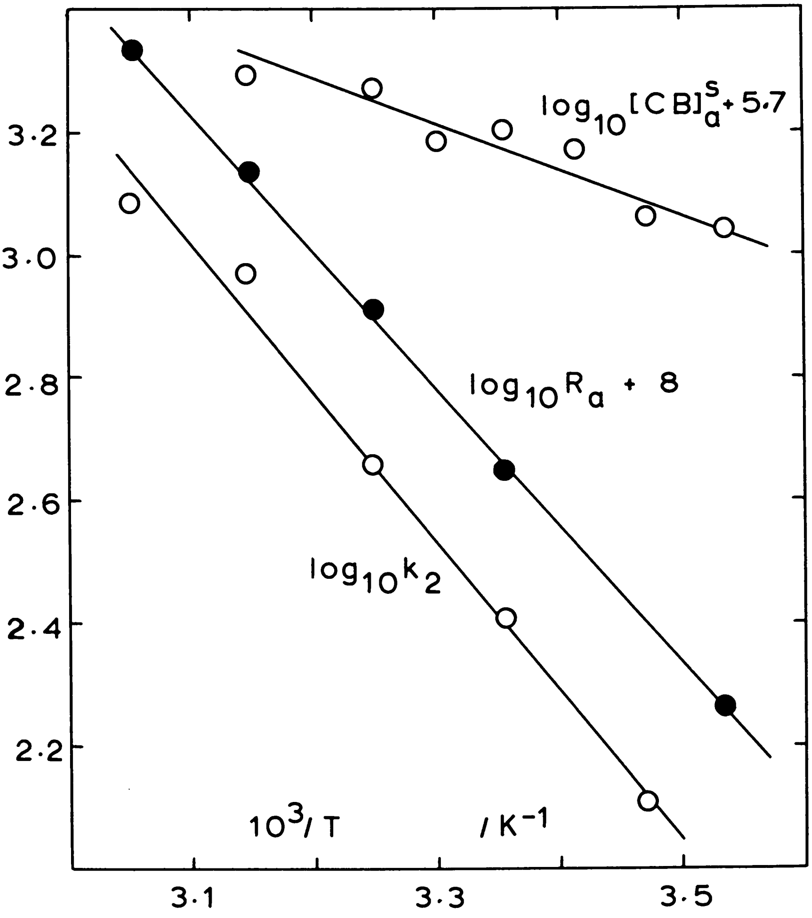
Arrhenius plots of the data are shown in the Figure and lead to E = 10,300, E_2 = 11,000 and ΔH_s = 3,100 cal mol^{-1}, where E and E_2 are the activation energies for the two phase and homogeneous nitration respectively, and ΔH_s is the heat of solution of chlorobenzene in the aqueous sulphuric acid.

Discussion

Comparison with Previous Data. The value of R_a at 25°C of 4.43 × 10^{-6} mol dm^{-3} s^{-1} is in excellent agreement with the value of 4.44 × 10^{-6} mol dm^{-3} s^{-1} obtained by Cox and Strachan (3) in the same apparatus and with the same nitric acid concentration

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch014

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch014



Arrhenius plots of R_a, k_2 and $[CB]_a{}^s$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch014

but using 79.8% H_2SO_4 and a stirring speed of 65 rpm. The value of 256 $dm^3\ mol^{-1}\ s^{-1}$ for k_2 at 25°C is larger by a factor of 2 that that predicted from an extrapolation of the linear relationship between log k_2 and % H_2SO_4 found by Schofield and coworkers over the range 67.5-77.4% H_2SO_4. This indicates that this linear relationship holds approximately but not exactly up to 80% H_2SO_4.

The value of E_2 of 11,000 cal mol^{-1} with 79.45% H_2SO_4 can be compared with values of 19,400 (2) and 16,970 (1) cal mol^{-1} with 67.5 and 70.2% H_2SO_4 respectively. It is in line with observations on other aromatics (2,4) that E_2 decreases by ~670 cal mol^{-1} for each 1% increase in sulphuric acid strength. Finally the solubility of chlorobenzene in 79.55% H_2SO_4 is slightly greater than in 70.2% H_2SO_4 in agreement with the observations of Deno and Perizzolo (5) and with the behaviour of benzene and toluene (6). The heat of solution is of the same order of magnitude as that observed at the lower sulphuric acid strength (1) and with benzene and toluene (6,7).

Predicted and Experimental Rates at 25°C. On the basis of previous work (3) in which the same nitric acid concentration was employed, a sulphuric acid strength of 79.8% should be well inside the fast reaction diffusional regime. The initial rate according to surface renewal theory (8) should therefore be given by

$$R_a = a' \sqrt{Dk_2[HNO_3]}\ [CB]_a^s \qquad (A)$$

where D is the diffusivity of chlorobenzene in the acid phase. From the dimensions of the cell and the volume of the acid phase $a' = 0.202\ cm^{-1}$. In 79.8% H_2SO_4 D is estimated to have the value $7.7 \times 10^{-7}\ cm^2\ s^{-1}$ (3). Direct experimental determinations of D for toluene (9) provide evidence that a value of D estimated in this way is unlikely to be greatly in error. The values of k_2 and $[CB]_a^s$ at 25°C in the Table were obtained at slightly different sulphuric acid strengths but must be close to those which apply at 79.8% H_2SO_4. Insertion in equation (A) of these values of a', D, k_2 and $[CB]_a^s$ and of $[HNO_3] = 0.56$ mol dm^{-3} leads to a predicted R_a of 6.75×10^{-6} mol $dm^{-3}\ s^{-1}$. Experimentally $R_a = 4.43 \times 10^{-6}$ mol $dm^{-3}\ s^{-1}$. While the agreement is not exact it is close enough to suggest that surface renewal theory and equation (A) account reasonably well for mass transfer rates under fast reaction conditions.

Predicted and Experimental Activation Energies. The temperature dependent quantities in equation (A) are D, k_2 and $[CB]_a^s$. The nitration rate R_a should therefore increase with temperature with an activation energy E given by

$$E = \tfrac{1}{2}(E_D + E_2) + \Delta H_s \qquad (B)$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch014

E_D being the activation energy for diffusion. In the modified Wilke-Chang equation (10), $D = \text{constant} \times T/\eta$ where T is the absolute temperature and η the viscosity of the medium. Experimental values of D for toluene (9) are, however, better fitted by

$$D \;=\; \text{constant} \times T/\eta^{0\cdot 8} \tag{C}$$

Insertion of the values of η for 80% H_2SO_4 over the temperature range 4.4 to 60°C (11) in equation (C) followed by a plot of log D versus 1/T leads to a value for E_D of 5,000 cal mol^{-1}. Combination of this value with those of E_2 and ΔH_s determined from the Arrhenius plots shown in the Figure leads via equation (B) to a predicted E of 11,100 cal mol^{-1}. This compares with an experimental E of 10,300 cal mol^{-1}. Again the agreement, although not exact, can be regarded as satisfactory.

Summary

The results obtained on nitrating chlorobenzene in a stirred cell with 0.56 mol dm^{-3} nitric acid in 79·8% H_2SO_4 are consistent with the rate being fast reaction mass transfer controlled. Reasonable agreement is obtained between the experimentally determined rate and activation energy and the values of these quantities predicted by surface renewal theory.

Acknowledgement

We are grateful to Hickson and Welch Ltd., Castleford, England for a Research Scholarship (for J.W.C.) and for help and interest in this work.

Notation

a'	interfacial area per unit volume of the acid phase, cm^{-1}
$[CB]_a^s$	solubility of chlorobenzene in the acid phase, mol dm^{-3}
D	diffusivity of chlorobenzene in the acid phase, $\text{cm}^2\ \text{s}^{-1}$
E	activation energy for two phase nitration, cal mol^{-1}
E_2	activation energy for homogeneous nitration, cal mol^{-1}
$[HNO_3]$	nitric acid concentration in the acid phase, mol dm^{-3}
ΔH_s	heat of solution of chlorobenzene in the acid phase, cal mol^{-1}
k	overall mass transfer coefficient, cm s^{-1}
k_2	second order nitration rate constant, $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$
R_a	nitration rate per unit volume of acid phase, mol $\text{dm}^{-3}\ \text{s}^{-1}$
T	absolute temperature, K
η	viscosity of the acid phase, cP

Literature Cited

1. Cox P.R. and Strachan A.N., Chem. Engng Sci. (1971) 26, 1013.
2. Coombes R.G., Crout D.H.G., Hoggett J.G., Moodie R.B. and Schofield K., J. Chem. Soc. (B), (1970), 347.
3. Cox P.R. and Strachan A.N., Proc. Int. Solv. Extr. Conf. (1974), 2415, Society of Chemical Industry, London.
4. Coombes R.G., Moodie R.B. and Schofield K., J. Chem. Soc. (B), (1968), 800.
5. Deno N.C. and Perizzolo C., J. Am. Chem. Soc. (1957) 79, 1345.
6. Cerfontain H. and Telder A., Rec. Trav. Chim. Pays-Bas (1965) 84, 545.
7. Cox P.R. and Strachan A.N., Chem. Engng Sci. (1972) 27, 457.
8. Astarita G., "Mass Transfer with Chemical Reaction", Elsevier, Amsterdam (1967).
9. Ismail H.A.M., Ph.D. Thesis, University of Bradford (1973).
10. Perkins L.R. and Geankoplis C.J., Chem. Engng Sci. (1969) 24, 1035.
11. Fasullo O., "Sulphuric Acid", McGraw-Hill, New York (1965).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch014

15

Some Aspects of Aromatic Nitration in Aqueous Systems

C. HANSON and M. W. T. PRATT

School of Chemical Engineering, University of Bradford, Bradford, England

M. SOHRABI

Institute of Chemical and Petrochemical Engineering,
Tehran Polytechnic, Tehran, Iran

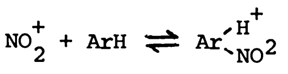
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

Aromatic nitration has been extensively studied and has played an important rôle in the development of theoretical organic chemistry. Most of the early published work, excellent reviews of which are available(1,2,3), has been concerned with nitration as a homogeneous liquid-phase reaction, usually with little or no water present. However, aromatic nitration is an important reaction in the chemical industry where it is commonly achieved by the use of an aqueous 'nitrating acid' mixture of 15 mole % nitric acid, 30 mole % sulphuric acid and 55 mole % water. The reaction is normally heterogeneous, the organic substrate and nitro product forming a separate phase from the aqueous acid. Published information about nitration in such aqueous systems has been relatively scant, although some attention has been given to them recently.

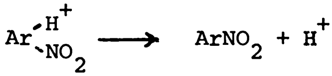
Ingold and his co-workers(4) proposed and firmly established a scheme now generally accepted for the mechanism of aromatic nitration with nitric acid or mixed nitric and sulphuric acids as nitrating agents, typically, in homogeneous solution in an organic solvent. In this the nitronium ion, NO_2^+, is the active intermediate which reacts with the aromatic compound, ArH:-

$$HNO_3 + H^+ \rightleftharpoons H_2\overset{+}{N}O_3 \qquad \text{(fast)} \qquad (1)$$

$$H_2\overset{+}{N}O_3 \rightleftharpoons NO_2^+ + H_2O \qquad \text{(slow)} \qquad (2)$$



$$NO_2^+ + ArH \rightleftharpoons Ar\begin{smallmatrix} H \\ NO_2 \end{smallmatrix}^+ \qquad \text{(slow)} \qquad (3)$$



$$Ar\begin{smallmatrix} H \\ NO_2 \end{smallmatrix}^+ \longrightarrow ArNO_2 + H^+ \qquad \text{(fast)} \qquad (4)$$

They also investigated the effect of water on the rate and order of the homogeneous reaction system. For reactive aromatic substrates, the reaction in the absence of water is zero order in aromatic concentration. This is because reaction (3) is much faster than the reverse of reaction (2). Nitronium ions are therefore consumed by reaction with the aromatic substrate as fast as they are formed. The rate controlling step is the production of nitronium ions by reaction (2), which is independent of the concentration and nature of the reactive substrate. Ingold and co-workers(5) found that water addition decreased the rate of reaction and ultimately caused a change from zero to first order kinetics in aromatic concentration. This was attributed to the effect of added water in increasing the rate of the reverse of reaction (2). The rate of reaction of nitronium ions with water becomes comparable with or greater than the rate of their forward reaction with aromatic substrate, so that the reactivity of the substrate becomes important and the rate of formation of nitro product involves both the concentration of substrate and nitronium ion. Similar observations were also made by Hoggett, Moodie and Schofield(6) during their studies of the relative reactivities of aromatic compounds.

The effect of water in depressing nitronium ion concentration was shown directly by Chédin(7) from the Raman spectra of mixtures of nitric acid, sulphuric acid and water, the Raman absorption band at 1400 cm^{-1} being attributed to the nitronium ion. Chédin's data were used to construct the triangular diagram, Figure 1, in which nitronium ion concentration is shown as a function of composition of the aqueous acid mixture. The diagram confirms the decrease in nitronium ion concentration with increase in the proportion of water. The limit of detectability of nitronium ion lies close to the line of Hetherington and Masson(8) representing the limiting acid strength for dinitration to occur and the composition of the usual 'mixed acid' used for industrial aromatic mononitrations lies in the region where nitronium ion is not detectable. Also shown on the diagram is the band obtained by Butt(9) representing the acid composition limits to the right of which detectable heterogeneous mononitration occurs within 5 hours at 20°C. Butt found that, for all three substrates, benzene, toluene and chlorobenzene, the band shown represented the nitration limit, allowing for experimental error of ± 2 mole %. Although the relative reactivities of these substrates to aromatic nitration are very different, the detection limit of nitro product under the given experimental conditions is reached within this narrow band of acid compositions, which represents acid mixtures with an aqueous proportion (approximately 90 mole %) far greater than those at which nitronium ions are spectroscopically detectable.

The experimental work described here was designed chiefly to provide more information, relevant to the aqueous nitration systems used industrially, concerning the effect of water on change in reaction order for a number of substrates and the

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

limiting acid compositions at which this occurs. A study was also made of the relative reactivities of aromatic substrates in homogeneous aqueous systems without the presence of organic solvents.

Effect of Water Addition upon Homogeneous Nitration by Nitric Acid

The effect of water addition on the nitration of toluene and some more reactive aromatic hydrocarbons in homogeneous solution in acetonitrile or acetic acid was studied at 20°C. Anhydrous nitric acid was used at first, no sulphuric acid being present, and then experiments were repeated with progressively higher initial concentrations of water. Nitric acid was always in large excess over the aromatic substrate concentration. For some experiments, fuming nitric acid was used.

Three different procedures were used to follow the reaction kinetics:-

For slow reactions with a half life of more than 30 minutes, reaction was carried out in 100 ml stoppered flasks, immersed in a thermostat with temperature controlled to $\pm$ 0.1°C. Each flask initially contained nitrating acid of known composition. After thermal equilibrium had been established, a measured volume of aromatic substrate, previously dissolved in organic solvent and immersed in the same thermostat, was added to the nitrating mixture. Samples were taken from the reaction vessel at intervals, diluted with solvent, and the absorbance of a suitable peak in the U.V. or visible spectra of the nitro products was measured by a Beckman double-beam spectrophotometer.

For faster reactions with a half life of less than 20 to 30 minutes, the procedure was the same, until after addition of the substrate to the nitric acid solution, following which the mixture was rapidly shaken to achieve a homogeneous solution. Part was transferred to a 1cm silica cell and the reaction followed at an appropriate wavelength in the spectrophotometer, of which the sample compartment was maintained at a controlled temperature by the circulation through surrounding coils of water from a thermostat.

Nitration by fuming nitric acid presented some difficulties, as the presence of free nitrous fumes causes some absorbance which overlaps with that of the 350nm peak of nitrotoluene. A correction was applied to the measured absorbance to allow for this, based upon the known specific absorbance of fuming nitric acid at the wavelength used.

Zeroth-order reactions were usually followed to completion and straight line plots of absorbance against time obtained up to at least 90% of the reaction. First or mixed-order reactions were generally followed to about three-quarters completion and rate constants were determined from the plot of log $(A_\infty - A_t)$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

TABLE I

Effect of water on the rate and order of the nitration of aromatic hydrocarbons by nitric acid in organic solvents at 20°C

Reaction conditions	[Substrate] mole l^{-1}	[H$_2$O] mole l^{-1}	Order	k_o mole l^{-1} sec^{-1} or k_1 sec^{-1}
Nitration of mesitylene by 7.41 mole l^{-1} HNO$_3$(a) in acetonitrile	0.0099	0	0	1.62×10^{-5}
	0.0171	0	0	2.00×10^{-5}
	0.0178	0	0	1.90×10^{-5}
	0.0198	0	0	1.65×10^{-5}
	0.0250	0	0	1.86×10^{-5}
	0.0171	0.125	0	1.32×10^{-5}
	0.0171	0.452	Mixed	$\sim 0.90 \times 10^{-5}$
	0.0171	0.986	Mixed	$k_1 \sim 9.90 \times 10^{-4}$
	0.0171	1.64	Mixed	$\sim 5.98 \times 10^{-4}$
	0.0171	1.97	Mixed	$\sim 3.18 \times 10^{-4}$
	0.0171	2.30	1	2.32×10^{-4}
Nitration of m-xylene by 7.41 mole l^{-1} HNO$_3$(b) in acetonitrile	0.0110	0	0	2.75×10^{-5}
	0.0304	0	0	2.60×10^{-5}
	0.0332	0	0	2.70×10^{-5}
	0.0304	0.130	0	2.20×10^{-5}
	0.0304	0.986	Mixed	$\sim 1.23 \times 10^{-5}$
	0.0304	1.64	Mixed	$k_1 \sim 2.10 \times 10^{-4}$
	0.0304	1.97	Mixed	$\sim 1.55 \times 10^{-4}$
	0.0304	2.15	Mixed	$\sim 1.12 \times 10^{-4}$
	0.0304	2.30	1	0.80×10^{-4}
Nitration of toluene by 8.895 mole l^{-1} HNO$_3$(a) in acetonitrile	0.0156	0	0	4.35×10^{-5}
	0.0217	0	0	4.40×10^{-5}
	0.0434	0	0	4.11×10^{-5}
	0.0434	0.132	0	2.38×10^{-5}
	0.0434	0.329	Mixed	$\sim 1.90 \times 10^{-5}$
	0.0434	0.658	Mixed	$\sim 1.18 \times 10^{-5}$
	0.0434	1.32	Mixed	$k_1 \sim 1.97 \times 10^{-4}$
	0.0434	1.64	Mixed	$\sim 1.54 \times 10^{-4}$
	0.0434	1.97	1	1.17×10^{-4}
Nitration of toluene by 7.41 mole l^{-1} HNO$_3$(a) in acetic acid	0.0125	0	0	7.12×10^{-5}
	0.0221	0	0	6.95×10^{-5}
	0.0444	0	0	7.00×10^{-5}
	0.0444	0.329	Mixed	$\sim 5.61 \times 10^{-5}$
	0.0444	0.986	Mixed	$k_1 \sim 12.10 \times 10^{-4}$
	0.0444	1.320	Mixed	$\sim 10.52 \times 10^{-4}$
	0.0444	1.64	1	8.42×10^{-4}

Table I continued overleaf

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

TABLE I (Continued)

Reaction conditions	[Substrate] mole l^{-1}	$[H_2O]$ mole l^{-1}	Order	k_0 mole l^{-1} sec^{-1} or k_1 sec^{-1}
Nitration of ethyl benzene by 7.44 mole l^{-1} HNO_3(a) in acetic acid	0.0186	0	0	6.70×10^{-5}
	0.0373	0	0	6.82×10^{-5}
	0.0405	0	0	6.76×10^{-5}
	0.0373	1.28	Mixed	$k_1 \sim 9.45 \times 10^{-4}$
	0.0373	1.603	1	8.81×10^{-4}

(a) $[HNO_2] \leq 1.44 \times 10^{-2}$ mole l^{-1}

(b) $[HNO_2] \leq 4.10 \times 10^{-3}$ mole l^{-1}

TABLE II

Conditions at point of change in reaction order from zero to first

Nitration conditions	$[HNO_3]$ mole l^{-1}	$[H_2O]/[HNO_3]$
mesitylene in acetonitrile, t = 20°C	7.41	0.31
m-xylene in acetonitrile, t = 20°C	7.41	0.31
toluene in acetonitrile, t = 20°C	8.89	0.22
toluene in acetic acid, t = 20°C	7.41	0.22
ethyl benzene in acetic acid, t = 20°C	7.44	0.21
N-methyl 2:4:6 tri-nitroaniline in nitro methane (a) t = 25°C	3.0	0.27

(a) Reference(5)

against time, in which A_∞ is the final absorbance, measured after a long time interval, and A_t is the absorbance at time t. For first-order reactions, the plots were straight lines of slope $-k_1/2.303$, where k_1 is the first-order rate constant. Mixed order reactions gave curves on both the zero and first-order plots.

Aromatic substrates studied in acetonitrile or acetic acid solutions were toluene, m-xylene, ethyl benzene and mesitylene and the results are shown in Table I. For all the systems containing no or very little water, a zeroth order kinetic law in substrate concentration was obeyed. As the concentration of water present initially was successively increased, the order ultimately became disturbed and finally a first-order law was established. Figures 2 and 3 show the changeover in reaction order for the nitration of toluene in acetonitrile solution.

The molar ratio of $[H_2O]/[HNO_3]$ at the region of change in reaction order was calculated for all the systems and is shown in Table II, together with the corresponding results given by Hughes, Ingold and Pearson(5) for the system n-methyl 2, 4, 6 tri-nitroaniline in nitromethane.

This 'changeover' molar ratio appears to be independent of the concentration of nitric acid and also of the organic solvent used and is surprisingly constant in the range 0.2 to 0.3. Variation with reactivity of the aromatic substrate is certainly only slight.

The ratio $[H_2O]/[HNO_3]$ at the changeover in order was also compared with the limiting composition of nitrating acid mixtures at which nitronium ions are just detectable by Raman spectroscopy. In Chédin's triangular diagram (Figure 1) the locus of zero intensity of the $1400 cm^{-1}$ Raman line of nitronium ion intercepts the water - nitric acid axis at a point which corresponds to about 94 wt% nitric acid, equivalent to a molar ratio $[H_2O]/[HNO_3]$ of 0.22. The close agreement between the molar ratios corresponding to changeover in reaction order and spectral disappearance of nitronium ion is striking. Recently, the location of the line of zero intensity for nitronium ion has been re-investigated by Zaman(10) using a laser beam Raman spectrophotometer. He obtained a line very close to that given by Chédin, confirming the earlier findings.

The Effect of Sulphuric Acid on Reaction Order

The effect of the addition of small quantities of sulphuric acid upon the reaction order with respect to substrate concentration was investigated. For toluene nitration in aqueous acetic acid, the addition of up to 0.218 mole l^{-1} of sulphuric acid increased the first-order rate constant greatly, but did not cause a reversion to zeroth order or mixed order kinetics. The same concentration of sulphuric acid disturbed the first-order nitration in acetonitrile of the more reactive

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

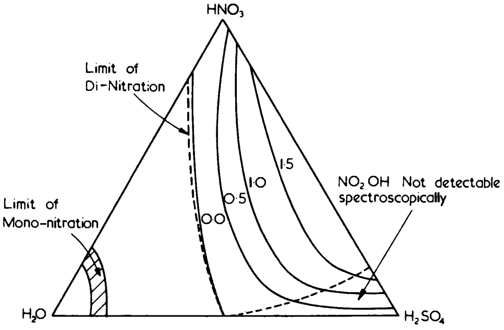


Figure 1. Nitronium ion (NO_2^+) concentrations (g ions/1000 g solution) in the system: nitric acid, sulfuric acid, water

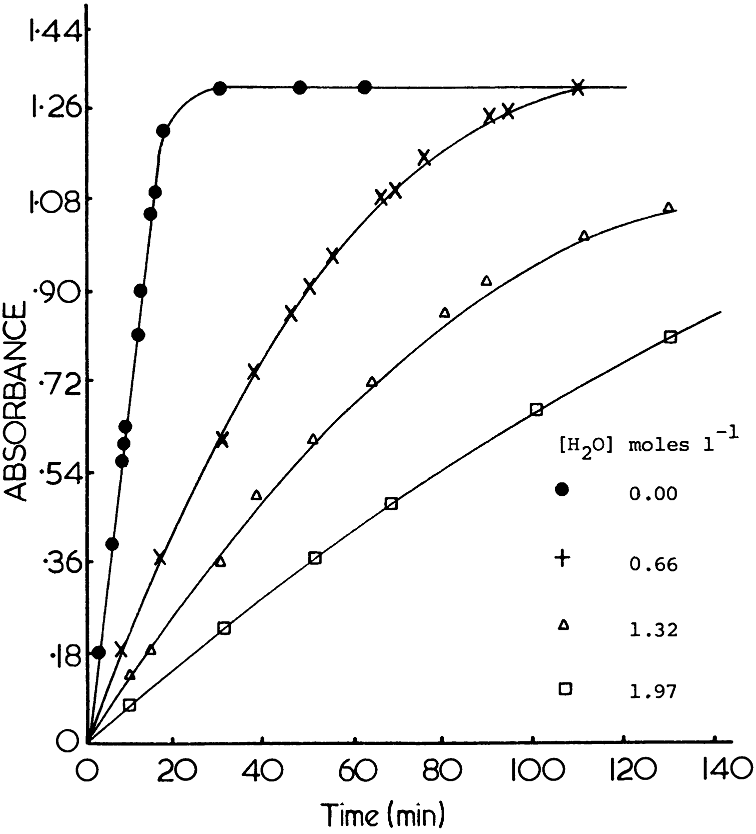


Figure 2. The effect of added water on the rate of nitration of toluene in acetonitrile

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

substrate mesitylene and, to restore first-order kinetics, a higher concentration of water had to be added. In Figure 4 is shown the effect of sulphuric acid concentration on $[H_2O]/[HNO_3]$ ratio at the change in reaction order. The initial substrate, nitric acid and water concentrations were those shown in Table I for these systems at the changeover region; the reaction temperature was again 20°C. For mesitylene, the composition of the sulphuric acid - nitric acid - water nitrating medium at the changeover in order runs almost parallel to and quite close to the zero intensity line for nitronium ion in Chédin's diagram.

Experiments with Fuming Nitric Acid

A few experiments were performed with solutions of fuming nitric acid in acetic acid as nitrating agent. The fuming nitric acid used contained 0.267 mole l^{-1} of free 'nitrous acid' and its nitric acid content was 95.5% ± 2%. Toluene nitration by these solutions and with nitric acid in constant excess over aromatic was dependent on substrate concentration to a power between zero and unity. The results given in Table III show that addition of water and nitrate ion reduces the rate of reaction and further increase in water concentration produces a reaction which is first order in toluene concentration. This is understandable, as both nitrous acid (nitrite ion) and nitrate ion repress aromatic nitration by deprotonating the nitric acidium ion, which is the precursor of the nitronium ion(4). For example, in the case of nitration in the absence of sulphuric acid, the reaction scheme given earlier is preceded by:- $HNO_3 \rightleftharpoons H^+ + NO_3^-$. This equilibrium will be driven back from right to left by nitrate ion and nitronium ion formation will be impeded.

Effect of Urea

Urea has an anti-catalytic effect on nitration(4,6) which Ingold attributed to the dissociation of urea nitrate in organic solvent to urea and nitrate ion, of which the rate depressing effect has already been mentioned. The nitrous acid content of the nitrating mixtures used previously to study this effect was always less than 10^{-3} mole l^{-1} and the added urea was always in large excess over nitrous acid. In the present investigation, the concentration of nitrous acid in the nitrating solutions containing fuming nitric acid was about 0.1 mole l^{-1}. The addition of successively increasing amounts of urea initially promoted the first-order rate of nitration of toluene, but a critical concentration was reached beyond which further addition of urea depressed the rate. Results for urea addition to toluene nitration by fuming nitric acid in acetic acid at 20°C are shown in Figure 5; the initial concentrations (mole l^{-1}) are:- nitric acid, 5.91; toluene, 0.195; and water, 0.97. The critical concentration of urea is, within experimental error, equal to

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

TABLE III

Effect of water on the rate and order of nitration of toluene by fuming nitric acid in acetic acid at 20°C

$[HNO_3]$ [(a)] mole l^{-1}	[Toluene] mole l^{-1}	$[H_2O]$ mole l^{-1}	k_1 sec^{-1}	Order
6.03	0.025	1.00	$\sim 14.30 \times 10^{-5}$	Mixed
5.91	0.195	0.97	$\sim 5.73 \times 10^{-5}$	Mixed
5.91	0.120	0.97	$\sim 4.60 \times 10^{-5}$	Mixed
5.91	0.197	1.27	$\sim 4.33 \times 10^{-5}$	Mixed
5.91	0.195	1.60	$\sim 3.51 \times 10^{-5}$	Mixed
5.91	0.195	1.91	2.86×10^{-5}	1
5.91	0.195	2.10	2.42×10^{-5}	1

(a) $HNO_2 \leq 0.267$ mole l^{-1}

Effect of nitrate ion on the rate of nitration of toluene by fuming nitric acid at 20°C

$[HNO_3]$ mole l^{-1}	[Toluene] mole l^{-1}	$[NaNO_3]$ mole l^{-1}	$[H_2O]$ mole l^{-1}	k_1 sec^{-1}
5.91	0.195	0	0.97	$\sim 5.73 \times 10^{-5}$
5.91	0.195	0.0244	0.97	$\sim 2.01 \times 10^{-5}$
5.91	0.195	0.0397	0.97	$\sim 1.53 \times 10^{-5}$
5.91	0.195	0.0244	1.91	0.96×10^{-5}
5.91	0.195	0.0397	1.91	0.75×10^{-5}

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

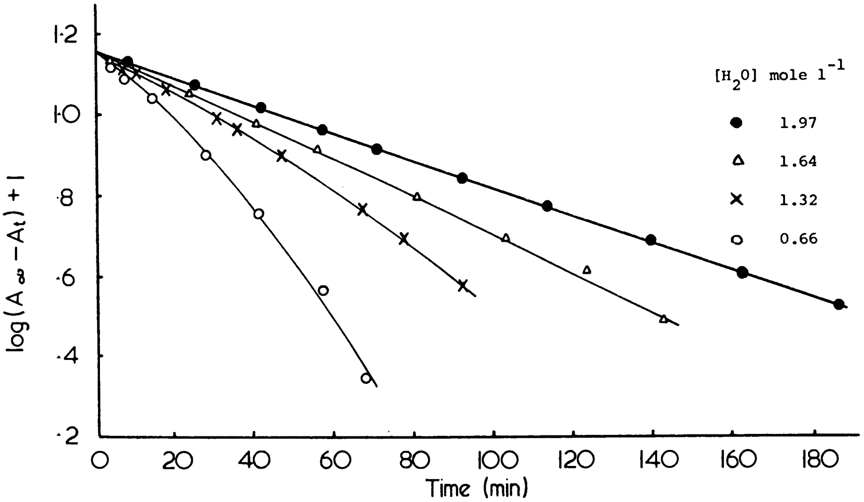


Figure 3. The effect of added water on the rate of nitration of toluene in acetonitrile

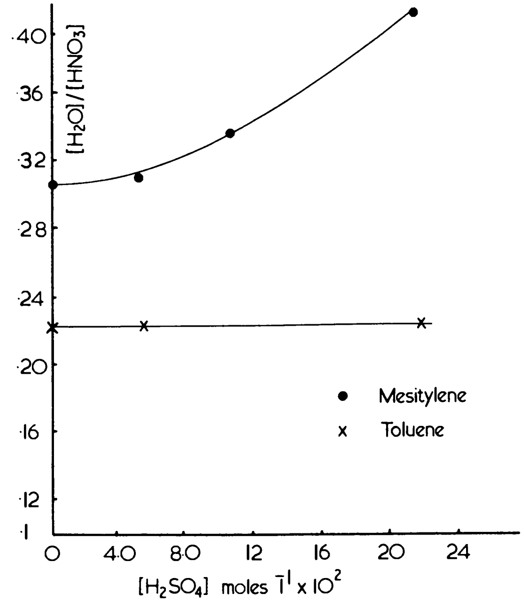


Figure 4. The effect of sulfuric acid on the $[H_2O]/[HNO_3]$ ratio at the change in order of reaction

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

half the molar concentration of nitrous species measured as nitrous acid which was present initially and corresponds to the complete removal of nitrous acid according to the reaction:-

$$CO(NH_2)_2 + 2\ HNO_2 = CO_2 + 3\ H_2O + 2\ N_2$$

This is understandable, as the depressing effect of nitrous acid on nitration rate has been noted earlier. The maximum rate is therefore achieved when sufficient urea has been added to destroy all the nitrous acid but excess urea is not present.

Nitration by Aqueous Nitric Acid

To investigate experimentally the kinetics of aromatic nitration at an intermediate situation between the homogeneous reactions in organic solvent considered so far, and the heterogeneous solvent-free systems used industrially, a study was made of homogeneous aromatic nitration carried out in the total absence of organic solvents. Reactions were followed at 25°C in aqueous nitric acid containing dissolved aromatic substrate. The solubilities of the aromatic compounds used (benzene, toluene, chlorobenzene, m- and p- xylene and mesitylene) were low in the aqueous acid media but the aromatic concentrations were sufficiently high for the reaction to be followed by spectrophotometer as before. In all cases, nitric acid was present in considerable excess over the aromatic compound. For all substrates, the nitration followed a psuedo first-order kinetic law.

The rate constants for each substrate were compared with those for benzene at the same nitric acid concentration to obtain relative reactivities for the substrates. Results are summarised in Table IV, and in Table V these reactivities are compared with those obtained by Hoggett, Moodie and Schofield(6) for nitration of the substrates in the aqueous organic solvents, Sulpholan and nitromethane. The agreement in relative rates is quite good and indicates that a similar reaction mechanism applies both with and without the presence of the organic solvents.

Heterogeneous Nitration of Toluene and Benzene

Industrial aromatic nitration, carried out heterogeneously with aqueous mixtures of nitric and sulphuric acids as nitrating agent, is an example of simultaneous mass transfer and chemical reaction, for the system forms two phases with the reactants distributed between them. For this type of system, either the chemical kinetics or the mass transfer process may limit the overall rate, depending on the reaction conditions. It is not our intention here to discuss the various mathematical models

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

TABLE IV

Pseudo first order rate constants (sec^{-1}) for the nitration of aromatic compounds at 25°C ± 0.1°

Substrate	[Substrate] mole l^{-1}	[HNO$_3$] mole l^{-1}	k_1 sec^{-1}	Rate relative to that of benzene
benzene	1.45×10^{-4}	13.5	0.47×10^{-4}	1
	1.87×10^{-4}	14	1.15×10^{-4}	1
	1.45×10^{-4}	14.5	3.07×10^{-4}	1
	1.57×10^{-4}	15	8.31×10^{-4}	1
toluene	1.32×10^{-4}	12.5	0.27×10^{-3}	
	1.45×10^{-4}	23	0.61×10^{-3}	
	1.51×10^{-4}	13.5	1.24×10^{-3}	26.3
	1.55×10^{-4}	14	2.74×10^{-3}	23.8
	1.23×10^{-4}	14.5	6.70×10^{-3}	21.8
chloro-benzene	1.42×10^{-4}	14.5	0.239×10^{-4}	0.0778
	1.24×10^{-4}	15	0.697×10^{-4}	0.0838
mesitylene	0.418×10^{-4}	12.5	4.03×10^{-3}	360
	0.342×10^{-4}	13	10.7×10^{-3}	418
	0.342×10^{-4}	13.5	21.2×10^{-3}	410
p-xylene	1.124×10^{-4}	12.5	2.40×10^{-3}	213
	0.753×10^{-4}	13	5.11×10^{-3}	199
	0.956×10^{-4}	13.5	11.4×10^{-3}	238
m-xylene	1.04×10^{-4}	12.5	1.82×10^{-3}	162
	1.08×10^{-4}	13	4.35×10^{-3}	170

TABLE V

Relative rates of nitration

Compound nitrated	Aqueous (a) Sulpholan	Aqueous (a) Nitromethane	Aqueous Nitric Acid	Estimated Relative Rates		
				Aqueous Sulpholan	Aqueous Nitromethane	Aqueous Nitric Acid(b)
chlorobenzene	-	-	0.08	-	-	(0.08)
benzene	1	1	1	(1)	(1)	(1)
toluene	20	25	24	(20)	(25)	(24)
m-xylene	100	146	165	1000	2350	2080
p-xylene	114	130	200	80	90	100
mesitylene	350	400	380	48,000	60,000	46,400

(a) Ref. (6)

(b) Calculated from the toluene:benzene ratio and isomer distribution in aqueous nitric acid

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

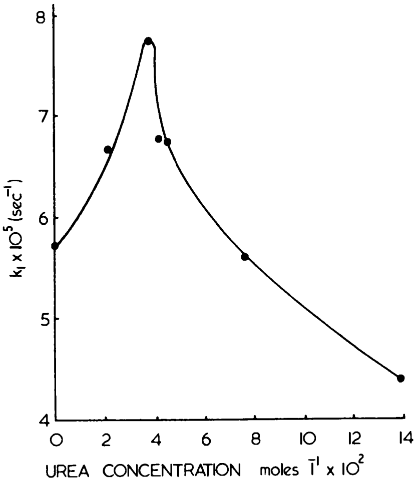


Figure 5. The effect of urea on the first-order rate of nitration of toluene by fuming nitric acid

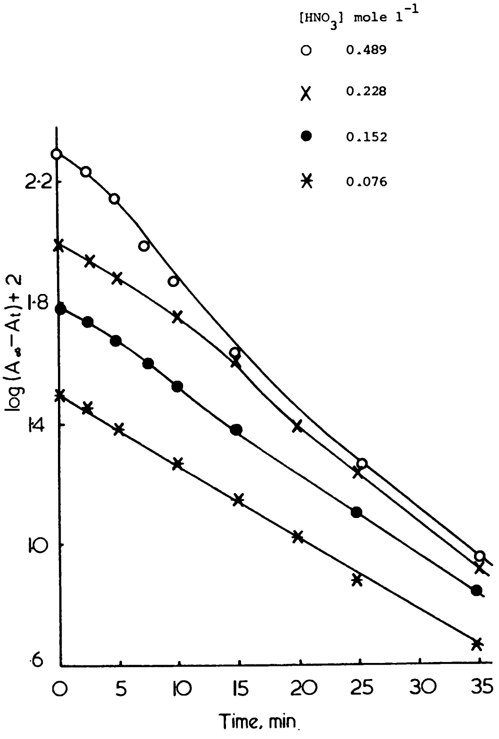


Figure 6. Two-phase nitration of benzene in 68.87% sulfuric acid at 25°C

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

which have been developed to describe mass transfer with chemical reaction as applicable to nitration systems; these are detailed elsewhere, for example, in contributions of Strachan and Hanson, with their co-workers, to this symposium. Some experiments were, however, performed which demonstrated the transition between mass transfer and chemical kinetic control during the heterogeneous nitration of benzene and toluene.

The reaction vessel used was a 500ml round-bottomed three-necked flask fitted with an agitator having a four blade turbine impeller, 0.5cm in diameter, rotating at a constant speed of 3,000rpm. The vessel was immersed in a thermostat at 25°C ± 0.2°C. To 200ml of aqueous sulphuric acid of known strength containing 0.01 to 0.5 mole l^{-1} nitric acid were added 200ml of the substrate at the same temperature. Samples were taken at regular intervals, chilled, washed with water, and the organic phase separated, centrifuged, and analysed spectrographically for the concentration of nitro product. Conditions were usually such that, initially, the concentration of nitric acid was high and the rate of chemical reaction was greater than that of mass transfer. The overall rate of production of nitro-product during this stage increased at first, possibly due to a decrease in interfacial tension, which causes an increase in interfacial area. Then the rate became approximately constant as a transition stage was approached during which the rate of mass transfer was approximately constant. Ultimately, the proportion of nitric acid consumed was high enough to reduce the chemical rate of reaction below that of the mass transfer process. When the chemical kinetics took over as the rate-determining step, the rate of production of nitro-product decreased according to a pseudo first-order law, the concentration of substrate being almost constant throughout the reaction and approximately equal to its solubility in the sulphuric acid; plots of $\log(A_\infty - A_t)$ then became linear. Figures 6 and 7 show the transformation between mass transfer and kinetic control during the nitration of benzene and toluene for differing initial concentrations of nitric acid. Where the plots of $\log(A_\infty - A_t)$ are linear, chemical kinetics are rate controlling, curved plots indicate the diffusion controlled and a transition region. If the initial concentration of nitric acid is low enough, the entire reaction is kinetically controlled.

General Discussion

The observation that the molar ratio $[H_2O]/[HNO_3]$ at the region of change of order of aromatic nitration from zero to first in substrate concentration is fairly constant and close to that of the spectroscopic detection limit of nitronium ions may raise the question of whether the nitronium ion mechanism, so firmly established for nitration in low aqueous systems, still

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

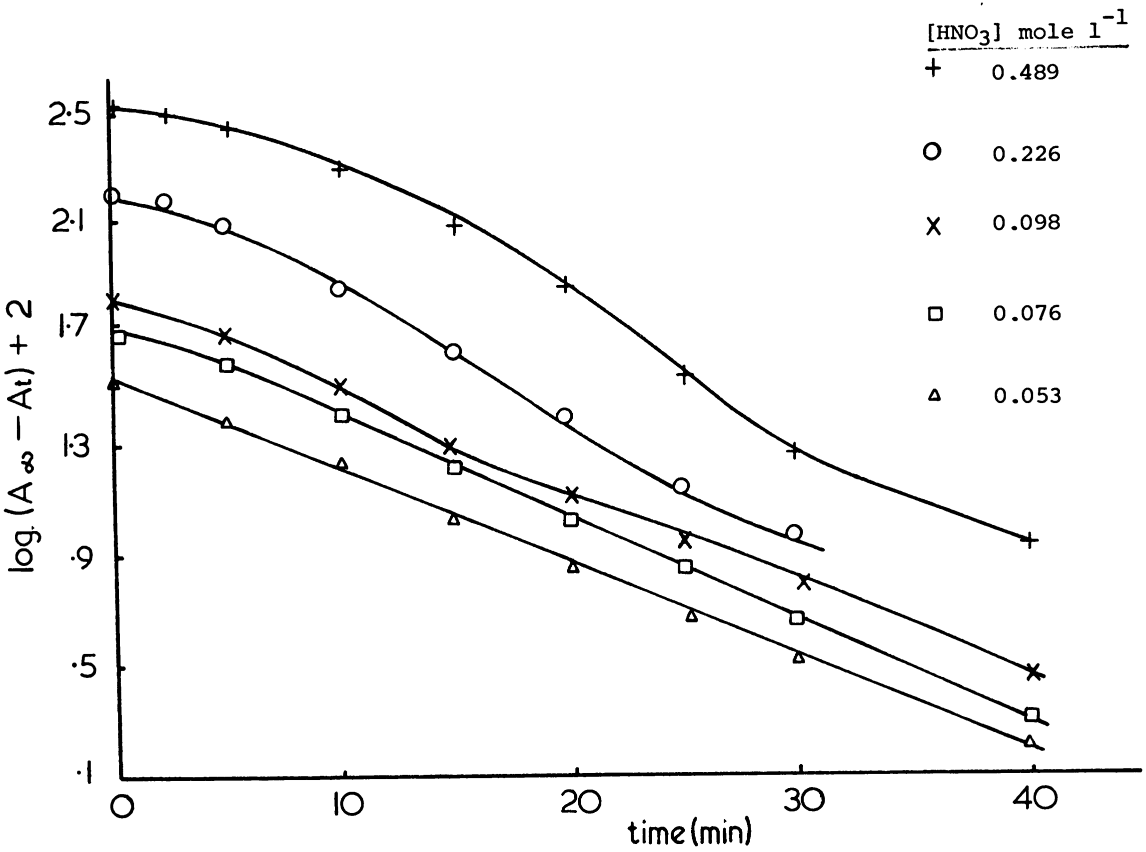


Figure 7. *Two-phase nitration of toluene in 67.7% sulfuric acid at 25°C*

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

applies to the highly aqueous sytems used industrially. As the ratio of $[H_2O]/[HNO_3]$ will be related to the equilibrium concentration of nitronium ions, it could be that the limiting value of this ratio represents a nitronium ion concentration which has fallen so low that another mechanism takes over; this concentration being the same as that at which the spectroscopic detection limit of nitronium ions is reached.

However, the general character of the results reported here is capable of explanation by the nitronium ion mechanism. Firstly, according to Ingold, the change from zero to first order is explained by increase in water concentration to the extent that reaction between nitronium ions and water competes with reaction between nitronium ions and the aromatic substrate. The reaction rate is then no longer independent of substrate concentration. As water concentration rises, first order behaviour would be expected to be shown first by substrates of low reactivity, for which the reaction with nitronium ions will be relatively less able to overwhelm the alternative reaction between nitronium ions and water. For a constant nitric acid concentration, therefore, weakly reactive substrates would be expected to show first order behaviour at a lower $[H_2O]/[HNO_3]$ ratio than highly reactive substrates. Such variation as has been found in the limiting $[H_2O]/[HNO_3]$ ratio for different substrates gives some support to this prediction, although the total variation is small.

Secondly, if the concentration of nitronium ion in the 68 wt % sulphuric acid nitrating mixtures used industrially is taken as being of the order of 10^{-8} moles l^{-1} and if reaction between nitronium ion and aromatic substrate is close to the encounter rate, it is quite possible to account for the observed rates of nitration, even though the assumed concentration of nitronium ions is well below their spectroscopic detection limit.

Further strong evidence for the nitronium ion mechanism in aqueous nitric acid of up to about 60 mole % water comes from the work of Bunton and co-workers(<u>12-15</u>). They studied the rate of ^{18}O exchange between water and nitric acid and found that the rate is approximately equal to the zeroth order rate of nitration of highly reactive aromatic compounds in these media. It was deduced that the exchange of oxygen occurred through heterolysis to produce the nitronium ion (reaction 2) which will have an equal rate to that of zeroth-order nitration. A possible point of criticism is that it is not absolutely clear whether the acid solutions used were positively shown to be free from nitrous acid. If any nitrous acid is present in nitrating acid, it can lead to nitration by means of nitrosation involving the NO^+ ion (<u>16</u>):-

$$ArH + HNO_2 \rightarrow ArNO + H_2O \text{ (slow)}$$

$$ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2 \text{(fast)}$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

Particularly liable to reaction through nitrosation are highly reactive substrates, the type used by Bunton. Correspondingly, reduction or elimination of nitrous acid can cause reaction via nitrosation to be redirected through the nitronium ion mechanism (6).

If any alternative to the nitronium ion mechanism for aromatic nitration were to be considered in aqueous systems, it would be most likely to involve the nitric acidium ion, which is accepted as the precursor of nitronium ion. The presence of nitric acidium ion, $H_2NO_3^+$, and also $H_3NO_3^{++}$, in aqueous solutions of nitric acid has been claimed in several papers based upon measurements of electrical conductivity, density and viscosity of nitric acid, sulphuric acid and water systems. These papers are summarised elsewhere(11). The effectiveness of the nitric acidium ion as a nitrating agent in 70% aqueous nitric acid has been claimed by Ward, Johnson and Day(17), who investigated the nitration of 1, 5 dinitro-naphthalene in several nitrating media, and suggested that a change from a nitronium ion mechanism in strong acid media to a nitric acidium ion in more aqueous media could account for the observed variation in isomer ratio of the tri-nitro product.

However, the nitronium ion in aqueous systems must surely be hydrated to some extent and the difference in kinetics to be expected between hydrated nitronium and nitric acidium ion will be related to the degree of bonding between water and nitronium ion and the moment in the reaction process at which the water molecule is released.

Thus, while the experimental results reported here raise points which we hope will be of interest, they cannot be held to disprove the belief that the nitronium ion mechanism applies to highly aqueous systems. Equally well, they do not definitely exclude the possibility that an alternative mechanism participates in these circumstances. Further work is necessary to clarify the question. Data of the type reported here but covering the effect of substrate concentration would be particularly valuable.

Conclusions

1. As water is added to the reaction system for the nitration of several reactive aromatic hydrocarbons by nitric acid or mixed nitric and sulphuric acids in acetonitrile or acetic acid solutions, the kinetics eventually change from zeroth to first order in concentration of the aromatic substrate. The molar ratio $[H_2O]/[HNO_3]$ at the region of change in order is similar for all the aromatic compounds studied and is close to that at which nitronium ions cease to be spectroscopically detectable.

2. The relative rates of aromatic nitration in 12-15 mole l^{-1} nitric acid in systems free from organic solvents are virtually the same as those in systems containing organic solvents and indicate that the controlling reaction mechanism is the same.

Literature Cited

1. Gillespie,R.J. and Millen,D.J., Quart.Rev.(1948) 2,277.
2. Ridd,J.H.,"Studies on Chemical Structure and Reactivity", Methuen & Co.Ltd.,London (1966).
3. Hoggett,J.G.,Moodie,R.B.,Penton,J.R. and Schofield,K., "Nitration and Aromatic Reactivity", Camb.Univ.Press (1971).
4. Hughes,E.D.,Ingold,C.K. and Reed,R.I., J.Chem.Soc. (1950), 2400.
5. Hughes,E.D.,Ingold,C.K. and Pearson,R.B., J.Chem.Soc. (1958) 4357.
6. Hoggett,J.G.,Moodie,R.B. and Schofield,K., J.Chem.Soc.(1969) 1.
7. Chédin,J., Compt.rend. (1935), 200, 1397.
8. Hetherington,J.A. and Masson,I., J.Chem.Soc. (1933) 105.
9. Butt,K.U., MSc Thesis, University of Bradford (1969).
10. Zaman,M.B., PhD Thesis, University of Bradford (1972).
11. Sohrabi,M., PhD Thesis, University of Bradford (1972).
12. Bunton,C.A.,Halevi,E.A. and Llewellyn,D.R., J.Chem.Soc.(1952) 4913.
13. Bunton,C.A. and Halevi,E.A., J.Chem.Soc. (1952) 4917.
14. Bunton,C.A. and Steadman,G., J.Chem.Soc. (1958) 2420.
15. Bunton,C.A.,Hughes,E.D.,Ingold,C.K.,Jacobs,D.I.,Jones,M.H., Minkoff,G.J. and Reed,R.I., J.Chem.Soc. (1950) 2628.
16. Olah,G.A.,Kuhn,S.J. and Flood,S.H., J.Am.Chem.Soc. (1961) 83, 4581.
17. Ward,E.R.,Johnson,C.D. and Day,L.A., J.Chem.Soc. (1959) 487.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch015

Nitration of Anthraquinone in Nitric Acid

F. W. EVANS and W. FREY
Sandoz Ltd., Basle, Switzerland

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

1-Aminoanthraquinone, an important intermediate for dyes and pigments, has been previously manufactured industrially by the mercury catalyzed sulphonation of anthraquinone followed by ammonolysis of the resulting sulphonic acid. To avoid the pollution problems inherent in this process, in particular the mercury contamination of the product and effluents, the obvious route of nitration (1, 2), followed by reduction of the 1-nitroanthraquinone, has been studied. In the following, the kinetic and reaction engineering results of the nitration of anthraquinone in nitric acid will be discussed.

Experimental kinetic studies.

When anthraquinone is added to concentrated nitric acid, 1-nitroanthraquinone is formed together with 2-nitroanthraquinone and various dinitroanthraquinone isomers. The microkinetics of the nitration were studied in the classical manner of carrying out reactions at constant temperatures in laboratory equipment. Samples of reaction mixture were withdrawn after given reaction times and these immediately added to an ice-water mixture. This dilution causes immediate stopping of the reaction and precipitation of the solid anthraquinone compounds. The resulting suspension was filtered, the filter cake washed, dried and then analysed by means of a gas chromatographic method developed in these laboratories.

The absolute concentrations (weight %) of anthraquinone, 1- and 2-nitroanthraquinone and the sum of all dinitroanthraquinone isomers were determined in each sample. At the time this kinetic study was carried out, we were unable to analyse the separate dinitro-isomers and consequently they were treated as one compound. We now know that the 1,5-, 1,8-, 1,6- and 1,7-isomers are formed in the ratio 40, 40, 10, 10 . The other six possible dinitroanthraquinone isomers and trinitroanthraquinone

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

compounds are not formed in detectable amounts, i.e. less than 0.3 weight %. Thin layer chromatographic analysis of the reaction products has shown that the amount of oxy-anthraquinone compounds formed through oxidation reactions is also very small (0 - 2 weight %). These side reactions have not been incorporated in our model.

A series of 21 experiments were carried out using technical grade anthraquinone and nitric acid. The following reaction parameters were varied in the ranges and with the accuracies given below:

- Weight ratio : nitric acid to anthraquinone	6:1 to 12:1	(± 0.1)
- Reaction temperature	0 to 20°C	(± 0.5°C)
- Water content of nitric acid (weight %-H_2O)	0.2 to 2.9	(± 0.05)
- Nitrous acid content of nitric acid (weight %-N_2O_3)	0.06 to 0.6	(± 0.03)
- Reaction time	0 to 180 min.	(± 0.5 min.)

The amounts of water and nitrous acid in the nitric acid were determined by titration of the acid with standard caustic soda and potassium permanganate solutions. We have assumed that the amount of nitrous acid remains constant during the reaction and is present in the form N_2O_3 (3). The results of a typical kinetic experiment are given in figure 1 .

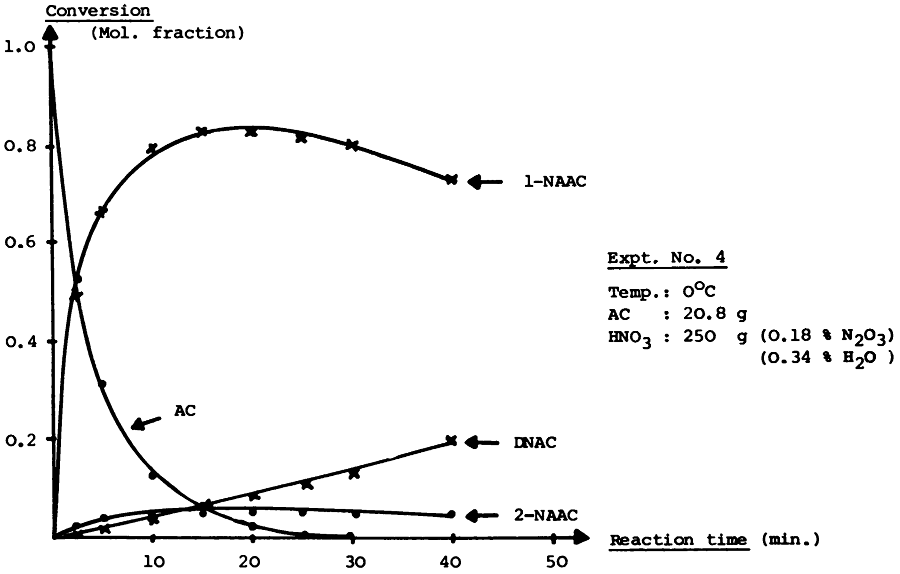


Figure 1. Typical kinetic experimental results

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

Kinetics of reaction.

Model. The following model is proposed for the nitration of anthraquinone in nitric acid:

Reactions

$$
\begin{aligned}
&\text{AC} + \text{HNO}_3 \xrightarrow{k_1} \text{1-NAAC} + \text{W} \\
&\text{AC} + \text{HNO}_3 \xrightarrow{k_2} \text{2-NAAC} + \text{W} \\
&\text{1-NAAC} + \text{HNO}_3 \xrightarrow{k_3} \text{DNAC} + \text{W} \\
&\text{2-NAAC} + \text{HNO}_3 \xrightarrow{k_3} \text{DNAC} + \text{W}
\end{aligned}
$$

Mass balance equations

$$
\begin{aligned}
[\text{AC}_\text{o}] &= [\text{AC}] + [\text{1-NAAC}] + [\text{2-NAAC}] + [\text{DNAC}] \\
[\text{W}] &= [\text{W}_\text{o}] + [\text{1-NAAC}] + [\text{2-NAAC}] + 2\,[\text{DNAC}] \\
[\text{N}_2\text{O}_3] &= \text{constant during the reaction}
\end{aligned}
$$

Kinetic equations

$$
\frac{d\,[\text{1-NAAC}]}{dt} = (\,k_1\,[\text{AC}] - k_3\,[\text{1-NAAC}]\,) \cdot F
$$

$$
\frac{d\,[\text{2-NAAC}]}{dt} = (\,k_2\,[\text{AC}] - k_3\,[\text{2-NAAC}]\,) \cdot F
$$

$$
\frac{d\,[\text{DNAC}]}{dt} = k_3\,(\,[\text{1-NAAC}] + [\text{2-NAAC}]\,) \cdot F
$$

$$
\text{where } F = e^{-P(7)\,[\text{W}] - P(8)\,[\text{N}_2\text{O}_3]} \cdot [\text{AC}_\text{o}]^{P(9)}
$$

$$
\begin{aligned}
k_1 &= e^{(P(1) - P(2)/T)} \\
k_2 &= e^{(P(3) - P(4)/T)} \\
k_3 &= e^{(P(5) - P(6)/T)}
\end{aligned}
$$

From the approximately 500 experimental numerical values the best values of the nine reaction parameters P(1)....P(9) were determined using a multivariant non-linear regression programme.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

For simplicity, the dimensionless units of mol. fraction conversions were used in the model instead of absolute values of the concentrations (conversion to 1-NAAC = $[NAAC]/[AC_0]$ etc.).

The values obtained were:

P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	P(7)	P(8)	P(9)
24.30	7262	25.17	8217	24.22	8115	1.165	12.85	-2.594

The standard deviation between the calculated and experimentally found values was 0.02, the maximum deviation was 0.115 .

Comments on the kinetic model. The proposed model has the following characteristics: With a given starting concentration of anthraquinone, the nitration reactions are first order with respect to the anthraquinone compounds and independent of the nitric acid concentration which is in large excess. The strong inhibiting effects of water and nitrous acid (N_2O_3) on the reaction rates are explained quantitatively by means of exponential functions. Neither the cubic relationships proposed by Ingold et. al. in their classical studies of nitration in nitric acid (4) or any other higher power function of the type $[\text{water}]^n$, $[N_2O_3]^m$ · can quantitatively explain the very large inhibiting effects of these two compounds over wide ranges of concentrations.

On the other hand, the effect of the starting concentration of anthraquinone can be interpreted by means of a power function, $[AC_0]^{P(9)}$. We belive that this unusual effect is caused by the formation of a chemical complex between the nitronium ion which is the effective nitration agent in nitric acid and all of the anthraquinone compounds in the reaction mixture.

$$2\ HNO_3 \overset{K_1}{\rightleftharpoons} NO_2^+ + NO_3^- + H_2O$$

$$2\ NO_2^+ + \text{AC-compounds} \overset{K_2}{\rightleftharpoons} \text{complex}$$

$$\text{Hence } [NO_2^+] = \frac{[\text{complex}]\ [NO_3^-]\ [H_2O]}{K_2 \cdot K_1 \cdot [\text{AC-compounds}]\ [HNO_3]^2}$$

With the assumption that the rate of reaction is proportional to some function of $[NO_2^+]$, it is not surprising to find the rate of reaction inversely proportional to the concentration of all anthraquinone compounds, i.e. proportional to $[AC_0]^{P(9)}$, with P(9) being negative.

Since completion of our studies, several patent publications concerning this nitration have appeared (5, 6). Using our model, we have simulated the reaction under the published conditions and compared the calculated results with those reported. The ranges

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

	This work	German Patent Publication 2 252 013	German Patent Publication 2 241 627 2 232 464
Weight Ratio (HNO_3/AC	6 - 12	3.6	0.91 - 15.1
Temperature (°C)	0 - 20	25 - 55	45 - 80
Reaction time (min.)	0 - 180	20 - 4320	0.5 - 40
Water in HNO_3 (wt. %)	0.2 - 2.9	3.6	2 - 3.6
Nitrous acid in HNO_3 (wt. 4)	0.06 - 0.6	? (= 0)	? (= 0)
No. of experimental points	172	3	24
Simulation Sum of squares of residuals	0.186	0.057	0.268
Standard deviation between simulation and reported values	0.019	0.08	0.103

Table I . Patent publications and model-simulations

Temp. (°C)	HNO_3/AC (wt. ratio)	H_2O (wt. %)	N_2O_3 (wt. %)	k_1F	k_1/k_2	k_1/k_3
0	12	0	0	.562	13.8	24.6
	12	3	0	.038	13.8	24.6
	12	0	.5	.175	13.8	24.6
	4	0	0	.047	13.8	24.6
50	12	0	0	34.58	8.05	15.2
	12	3	0	2.34	8.05	15.2
	12	0	.5	10.8	8.05	15.2
	4	0	0	2.91	8.05	15.2

Table II . Comparison of rate constants under various conditions

of reaction conditions given in these examples and a summary of the differences between simulated and published results are given in table I . The concentration of nitrous acid during the reaction is not given in these publications, consequently we have assumed a zero value for this variable. It can be seen that the model is able to predict the end products of reaction with a reasonable degree of accuracy under a very wide range of conditions, including those far removed from our experimental conditions.

Given the values of the kinetic constant parameters P(1)....

....P(6) one can calculate the best conditions for obtaining maximum yields of 1-nitroanthraquinone. As the activation energy for the formation of this compound is lower than the activation energies for the other two reactions the process should be carried out at as low a temperature as possible (table II).

Reactor design.

For the industrial application of this nitration the design of the reactor is of utmost importance. The reaction must be carried out under controlled conditions so that the amount of main product produced in the reactor is a maximum. Because of the potentially hazardous nature of the reaction and the necessity of rapidly stopping the reaction after a given degree of nitration, only a continuous type of reactor can be used in a large plant.

Ideal tubular reactor. The simplest type of continuous reactor is the tubular reactor operating under the condition of plug flow (7), consequently we developed a computer simulation programme for this type of reactor. The model included the three kinetic and two mass balance equations together with a differential equation for the heat balance (increase of temperature) along the reactor. The model was tested by carrying out simulations under the isothermal conditions (heat of reaction zero) used in the kinetic studies. Then, using a measured value of the heat of nitration (36 kcal mol^{-1}), we calculated the end products obtainable with the plug flow adiabatic reactor. A typical reaction product would be: AC 4.0 weight %, 1-NAAC 79.0 %, 2-NAAC 6.5 %, DNAC 10.5 %.

Cascade of stirred-tank-reactors. Our first pilot plant experiments were carried out in an existing cascade reactor system consisting of 4-stirred vessels with volumes of 0.25, 3.07, 3.04 and 3.17 litres coupled together in series. Each vessel was equipped with a cooling system, thus the temperature of each tank could be varied as desired. Residence time distribution studies of this system had shown that, under the conditions of interest, the flow characteristics of each tank were those of an ideal stirred tank (7).

The nitration was carried out by pumping nitric acid of known concentration and temperature at given rate (28 liter/hour) continuously through the cascade and adding anthraquinone by means of a weigh-belt feeder at a rate of 1.38 kg/hour to the first vessel. The reaction mixture leaving the last vessel and any samples taken from either of the vessel, were immediately diluted with ice-water to stop further reaction. These samples were then treated and analysed as described in section 2 .

A computer programme was written which simulated the nitration in a series of n-stirred tanks. With given conditions

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

Experiment No. 14: AC : 0.023 kg $min.^{-1}$
HNO_3: 0.28 kg $min.^{-1}$ (H_2O = 1.0 wt.%, N_2O_3 = 0.8 %)

Vessel No.	Temp. in vessel (°C)	Product-analysis (mol. %)				
			1-NAAC	2-NAAC	DNAC	AC
1	- 4.9	Expt.	5	1	0	93
		Model	5.5	0.7	0	94
2	3.0	Expt.	48	8	1	35
		Model	54	7.4	2.5	36
3	6.6	Expt.	71	6	8	25
		Model	72	9.7	7.2	11
4	7.2	Expt.	77	10	8	6
		Model	74	10	13	3.4

Table III . Nitration in a cascade of 4 stirred tanks

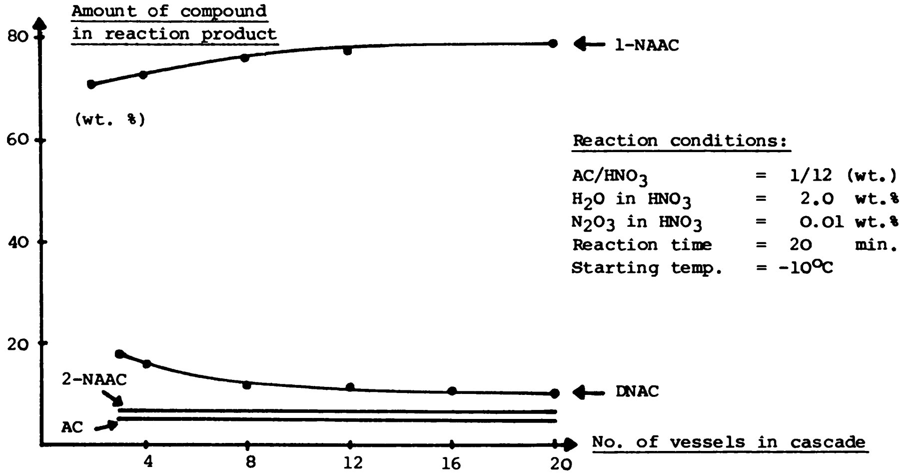


Figure 2. Stimulation of nitration in cascade reactor

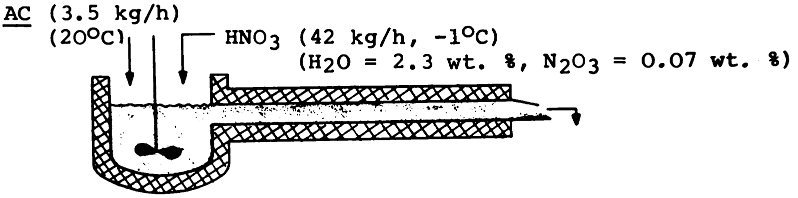
(flow rates, composition of nitric acid, temperatures and volumes of each tank) the programme calculated the composition of the reaction product in each tank in turn, starting with tank 1 .

Some of the results obtained experimentally are compared in table III with those predicted by the model. The agreement is excellent and, as expected, the amounts of dinitroanthraquinone formed in this reactor system are higher than in the plug flow reactor. Using this model we were able to show that for this nitration a cascade of at least 20 stirred vessels are required in order to obtain the same product-mixture as with the ideal tubular reactor (fig. 2).

Final pilot plant reactor. Following the sucessful operation of the cascade reactor, a new pilot plant was designed and used. In this reactor the nitric acid and anthraquinone were fed continuously at given rates into a stirred tank vessel (internal volume 1.3 liter) and the overflow from this vessel was allowed fo flow continuously through a tubular reactor (internal volume, 3.98 liter, diameter 15.8 mm) and then immediately diluted with water to stop the reaction. Samples of this suspension were filtered, dried and analysed as previously described. Both stirred tank and tubular vessel were well insulated, i.e. the reaction was carried out adiabatically.

In order to improve the flow characteristics through the tubular reactor, 10 lengths (each 50 cm) of static mixer elements were inserted at 100 cm internals along the tube. Residence-time distribution studies using a pulse of potasium chloride as tracer showed that this tubular reactor had the flow characteristics equivalent to a cascade of 35 stirred tanks in series. Thus for practical purposes, this tube can be considered to have flow characteristics equivalent to those of a plug flow reactor.

We have simulated the complete (stirred tank and tube) reactor system by combining our model for the cascade reactor, with only one stirred tank, with the model for the adiabatic ideal tubular reactor. An example of the excellent fit between simulated and experimentally found results is given in fig. 3 .



		Temp. (°C)	Product-analysis (wt. %)			
			AC	1-NAAC	2-NAAC	DNAC
In stirred tank	measured	7.3	70	26	2.8	0.9
	calculated	7.0	73	24.6	1.9	0.4
At end of reactor	measured	28.1	8.4	75.1	6.6	6.3
	calculated	30.3	6.3	78.1	6.8	8.7

Figure 3. Pilot plant reactor (adiabatic)

With this reactor system we have been able to achieve our goal of obtaining the product-mix of the ideal tubular reactor.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

Finally, a sensitivity analysis of this reactor system was carried out using the results of a series of simulations. This showed that the following limits of operating conditions must be maintained,in order to maintain the concentration of anthraquinone at the end of the reaction within the range of 2.5 - 4.5 weight %.

a) Temperature of imput nitric acid: limits ± 0.35°C

b) Nitric acid/anthraquinone ratio : limits ± 0.35 (weight basis)

c) Water content in nitric acid : limits ± 0.04 weight %

d) N_2O_3-content in acid : limits ± 0.01 weight %

e) Flow of nitric acid
(resisdence time): limits ± 5.8 volume/hour %

Our experience with the pilot plant showed that it was very difficult to maintain this required degree of consistency. It was therefore necessary to devise a special control system for this reactor and we hope to report on the use of the model in developing this controller at a later date.

Conclusion

An empirical mathematical model for a nitration which involves both simultaneous and consecutive reactions has been obtained from simple experiments. The model has been used to simulate various types of nitration reactors. These simulations are invaluable in predicting, correlating and understanding the results obtained from the various reactors.

Acknowledgment

The authors thank the following persons who have cooperated and assisted in this work: H. Frey, H. Link, W. Prikoszovich, W. Reinberg, H. Till, I. Toth and A. Zingg.

Notation

AC : anthraquinone
1-NAAC: 1-nitroanthraquinone
2-NAAC: 2-nitroanthraquinone
DNAC : dinitroanthraquinone, all isomers
W : water
N_2O_3 : nitrous acid in nitric acid (as N_2O_3)

$[AC_o]$: starting concentration of anthraquinone

$[W_o]$: starting concentration of water

$[AC]$, $[1\text{-}NAAC]$, etc.: concentration in $gmol.l^{-1}$

Literature cited

(1) Toth I., German Patent Publication (DOS) 2 162 538, Sandoz AG
(2) Graham D.E., Hort E.V., US-Patent 2 874 168 (1959)
(3) Hoggett J.G., Moodie R.B., Penton J.R., Schofield K., Nitration and Aromatic Reactivity, Cambridge Univ. Press (1971)
(4) Hughes E.D., Ingold C.K., Reed R.I., J.Chem.Soc. (1950), 2400
(5) German Patent Publication (DOS) 2 252 013, Ciba-Geigy AG
(6) German Patent Publication (DOS) 2 232 464 and 2 241 627, Bayer AG
(7) Dengigh K.G., Turner J.C.R., Chemical Reactor Theory, Cambridge Univ. Press (1971).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch016

17

Low Temperature Process for TNT Manufacture
Part 1. Laboratory Development

MARION E. HILL, CLIFFORD L. COON, WILLIAM G. BLUCHER,
GERALD J. McDONALD, CHESTER W. MARYNOWSKI,
WESLEY TOLBERG, HOWARD M. PETERS,
ROBERT L. SIMON and DONALD L. ROSS

Chemistry Laboratory, Stanford Research Institute, Menlo Park, Calif. 94025

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

Current processes for the manufacture of trinitrotoluene (TNT) produce atmospheric and water pollution that is only partly relieved by mechanical clean-up methods. TNT is currently produced from toluene by successive mono-, di-, and trinitrations with mixed aqueous nitric and sulfuric acids in the first two steps and anhydrous mixed acid in the last. Each stage in the current process is conducted at elevated temperatures, and side reactions in the overall process directly produce thousands of pounds of oxides of nitrogen, sulfuric acid aerosols, and volatile nitro organic products (such as tetranitromethane and nitroaromatics). These pollutants derive from the thermal decomposition of the aqueous nitric acid solutions, from oxidative side reactions that produce as many as 40 by-product compounds, and from formation of unsymmetrical "meta" isomers. Since symmetrical TNT is inevitably accompanied by meta isomers as well as oxidation products, the crude material is treated with sodium sulfite solutions to remove the undesirable isomers and nitroaromatics by derivatization. The spent sulfite solution, known as "red water," is then disposed of by combustion to an inorganic ash, itself a disposal problem.

We concluded that TNT production pollution could be alleviated by improving the chemical reactions that would obviate the decomposition of nitric acid, the oxidative side reactions, and the formation of unsymmetrical isomers. The practical constraints were to achieve the technical solution by a process that was economical, proceeded rapidly and in high yields, and was applicable to large scale production.

Voluminous literature reports aromatic nitration studies in various modes of mixed aqueous sulfuric and nitric acids. The reported nitration media were consistently used under conditions that produced oxidation as well as nitration, with nitration

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

being studied in most detail (1). Relatively little work had been reported on nitration in the very strong acid systems that should be nonoxidative and heat stable. Consequently, we decided that little could be gained by restudying methods similar to those already reported and sought an essentially new approach that would take advantage of toluene reactivity and milder conditions.

In previous work, we had developed a nitration medium of nitrate salts (such as sodium nitrate and potassium nitrate) in oleum that was stable at 140°C, highly reactive, and nonoxidative on the substrate tribromodinitrobenzene (2). Application of a similar mixture to the nitration of toluene under mild conditions revealed that dinitrotoluene was produced quantitatively in one step at room temperature. Subsequent work on equivalent anhydrous mixed acid systems produced similar results at temperatures as low as -13°C. Only nitration of dinitrotoluene to TNT required elevated temperatures and very strong acid.

Nitration of Toluene

Anhydrous Mixed Acid Systems. Although the initial experiments with nitrate salts produced quantitative yields of dinitrotoluene (DNT), there seemed to be no practical way to recycle acids or utilize the corresponding sulfate salt by-products. This consideration led us to try a mixed acid system that was equivalent to the salt mixtures in nitronium ion concentration. The mixed acid system was prepared essentially by dehydrating nitric acid with oleum and producing nitronium bisulfate and sulfuric acid:

$$HONO_2 + SO_3 \xrightarrow{H_2SO_4} NO_2HSO_4 + H_2SO_4$$

This reagent in 100% H_2SO_4 dinitrates toluene in over 99% yield as rapidly as the reactants can be mixed, at temperatures between 0°C and the freezing point of the nitrating solution:

$$C_6H_5CH_3 + 2\ NO_2HSO_4 \xrightarrow{-10^oC} \underset{\text{DNT}}{CH_3C_6H_3(NO_2)_2} + 2H_2SO_4$$

The dinitration was nearly quantitative under optimum conditions but was appreciably influenced by the mole ratios of HNO_3, SO_3, and toluene. When stoichiometric or excess SO_3 was present, yields of DNT were lower probably because of sulfonation of the ring. Best results were achieved with SO_3 slightly less than

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

stoichiometric (Figure 1). The medium produced by these concentrations was essentially NO_2HSO_4 dissolved in anhydrous sulfuric acid.

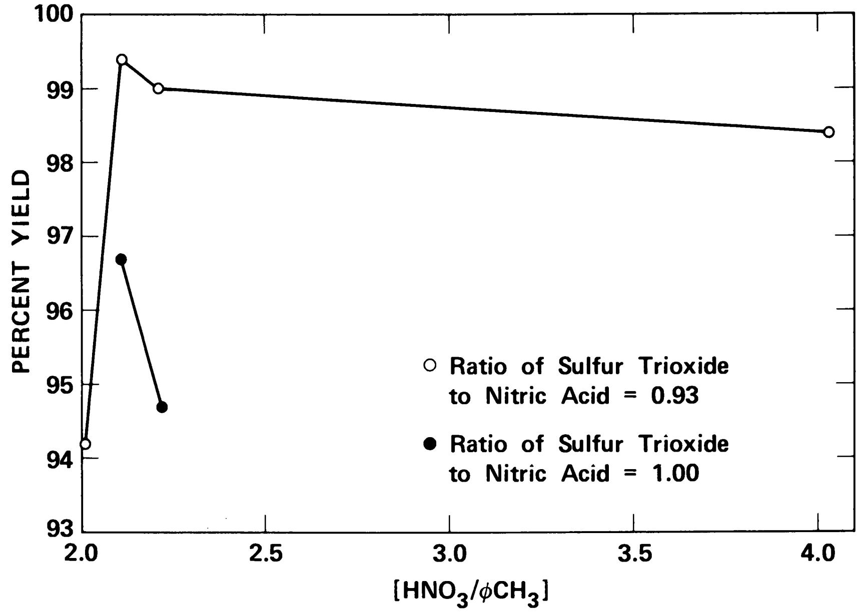


Figure 1. DNT yield as a function of nitric acid/toluene ratio at two nitric/SO_3 ratios

Current methods for nitrating toluene employ large excesses of nitric acid in aqueous media. Under the conditions of our experiments, however, only a slight excess of nitric acid to toluene (2.1 to 1 or 2.2 to 1) is necessary to ensure DNT yields of 99%. As the ratio of nitric acid to toluene is increased to 4 to 1, the DNT yield decreases slightly to ~ 98%. The optimum molecular proportion of reagents for the DNT step was toluene, 1.00; HNO_3, 2.11; and SO_3 (as 20% oleum), 1.97; this proportion results in a HNO_3/toluene ratio of 2.11 and a SO_3/HNO_3 ratio of 0.93. The yield of DNT obtained at -10°C was 99.4%.

Because nitration in a meta position occurs almost entirely in the mononitration step, factors that decrease meta nitration of toluene will eventually affect the final meta isomer content of

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

TNT. For example, nitration of either pure o- or p-nitrotoluene to DNT and then to TNT produced a product containing less than 0.1% meta isomers. Trinitration of pure 2,4-DNT gave no detectable meta-TNT isomers.

The most effective method for decreasing nitration in the meta positions of toluene is to lower reaction temperature. Dinitrations of toluene carried out at 40°C or higher always give at least 3.5% meta isomers. Positional selectivity toward less meta nitration increases as the reaction temperature is lowered; at -10°C only 1.8% meta isomers are formed. Lowering reaction temperature also changes positional selectivity in favor of 2,4 over 2,6 nitration; for example, the 2,4/2,6 ratio at -5°C was 6.27, while at -35°C this ratio was 9.62. Although lower reaction temperatures result in still lower percentages of meta isomers, -10°C appears to be the lower limit for an economically feasible process. At -18°C for example, the oleum-nitric acid mixture begins to thicken and having a high viscosity it becomes increasingly difficult to maintain a well-stirred, homogenous mixture. Brine solutions can be used for a -10°C reaction temperature, but the costs associated with maintaining lower temperatures become prohibitive.

Solutions of metal nitrate salts in oleum are also effective nitrating media for converting toluene to DNT, but they are neither as economical nor as convenient as the anhydrous nitric-sulfuric acid mixture. The active nitrating agent for the nitrate salt solution is probably NO_2HSO_4, just as in the nitric-sulfuric acid system.

$$MNO_3 + SO_3 + H_2SO_4 \xrightarrow{H_2SO_4} NO_2HSO_4 + MHSO_4$$

The nitrating solutions were prepared by saturating 15% fuming H_2SO_4 with the metal nitrate at ambient temperatures. However, the salts were not soluble enough to react with all the SO_3 (as $H_2S_2O_7$) according to the above equation. Consequently, SO_3 was present to compete as a reactant with the nitrating agent. The nitrating solutions prepared from $NaNO_3$ contained 14.2% NO_2HSO_4 and 5.7% SO_3; with KNO_3 there was 20.2% NO_2HSO_4 and only 1.5% free SO_3. Both systems readily nitrated toluene to DNT at -10°C, in 97% yield with KNO_3 and in 88% yield with $NaNO_3$. The higher yields obtained with the KNO_3 system were attributed to the lower concentration of SO_3.

Aqueous Mixed Acid Systems. Although anhydrous systems appear to be optimum, excellent dinitration results were obtained

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

in media composed of nitric and sulfuric acids and up to 7% water (3). These mixtures are equally as effective as the oleum-nitric acid mixtures in converting toluene to DNT in yields greater than 99% in 1 hr. The decrease in nitration in the meta positions showed the normal reaction temperature dependence and ranged from 2.06% at -5°C to 1.40% at -35°C, as shown in Table I. The temperature dependence for positional selectivity of 2,4- over 2,6-DNT follows the same trend as in the anhydrous systems.

Table I

TEMPERATURE DEPENDENCE OF ISOMER DISTRIBUTION AND SET POINT OF THE DINITROTOLUENE PRODUCT*

Reaction	DNT Isomers, %				Total	Set Pt.,
Temp., °C	2,4-	2,6-	3,4-	2,3- + 2,5-	Meta, %	°C
-5	84.48	13.46	1.41	0.65	2.06	61.0
-15	85.34	12.83	1.29	0.53	1.82	61.8
-25	85.47	11.77	1.26	0.50	1.76	62.5
-35	88.98	9.62	1.07	0.33	1.40	63.7

---

* $H_2SO_4/HNO_3/H_2O$ weight ratio, 90.6/6.3/3.1; HNO_3/toluene ratio, 4/1.

When water concentrations were allowed to exceed 7%, the reaction rate was considerably reduced, and complete dinitration was not obtained at low reaction temperatures. The DNT was accompanied by mononitrotoluenes (MNT) in varying ratios, depending on the amount of water present. At a sulfuric acid concentration of 80%, it was not possible to limit the reaction to mononitration except at low temperatures. At 70% sulfuric acid concentration, dinitration and mononitration occurred unless the nitric acid concentration was held to 5% or less. At sulfuric acid concentrations between 40% and 60% mononitration was readily achieved, and very little dinitration occurred.

Even at low temperature, however, aqueous nitration media produce more meta substitution. The amount formed depends more on water concentration than on either sulfuric or nitric acid concentrations. At a constant water concentration, variations in the sulfuric/nitric acid ratios result in little change in meta isomer formation. In all aqueous media experiments, the meta isomers ranged between 3% and 5% in the isomer distribution. We can conclude therefore that conditions sufficient for mononitration (as in current plants) but not for dinitration are also conditions for high meta formation; acid strengths sufficient for dinitration reduce meta concentrations.

Nitronium Trifluoromethanesulfonate. Another interesting method for the preparation of either MNT or DNT from toluene is the use of trifluoromethanesulfonic acid (TFSA) and nitric acid (4,5,6). The main interest in this medium is its ability to nitrate at extremely low temperatures to products that contain very low concentrations of meta isomers.

Two equivalents of TFSA and one of anhydrous nitric acid combine to form a white crystalline solid. This reaction can be carried out between the neat reactants or in solvents such as CH_2Cl_2, CCl_4, H_2SO_4, or excess TFSA itself. The solid is very hygroscopic, melts at 60-65°C, and partially sublimes at 60-70°C (1-2 mm). Elemental analysis and Raman spectroscopy showed it to be a mixture of nitronium trifluoromethanesulfonate (NTFS) and hydronium trifluoromethanesulfonate; structure assignment was confirmed in later work by Effenberger and Geke (6).

$$2CF_3SO_3H + HNO_3 \longrightarrow NO_2^+CF_3SO_3^- + H_3O^+CF_3SO_3^-$$

Nitronium trifluoromethanesulfonate proved to have excellent nitrating properties in each reaction medium investigated.

$$ArH + xNO_2CF_3SO_3 \longrightarrow Ar(NO_2)_x + xCF_3SO_3H$$

Product yields were nearly quantitative in reaction times of 1 to 60 minutes in a variety of solvents including sulfuric acid, TFSA, aqueous TFSA, methylene chloride, and $CFCl_3$, thus indicating the absence of side reactions. In sulfuric acid or mixtures of sulfuric acid and TFSA, dinitration of toluene by the nitronium salt gave high yields of DNT. In aqueous TFSA, as in aqueous sulfuric acid, either mono- or dinitration could be made to occur depending on the concentration of the acid.

Although it is not surprising that NTFS is an effective nitrating reagent in sulfuric acid, TFSA, or aqueous solutions of these acids, it has also proved to be an exceptionally good nitrating system in inert organic solvents. In organic solvents, mono- or dinitration of toluene can be controlled by reaction temperature. At -110° to -60°C in methylene chloride, mononitration was accompanied by only a trace of DNT products; at 0°C, or higher, quantitative yields of DNT were obtained. At -30°C mixtures of MNT and DNT were formed. NTFS, needed in only slight

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

stoichoimetric excess, proved to be only slightly less effective in carbon tetrachloride and pentane at 0°C and below.

The mononitration of toluene is very fast in all solvent systems, occurring within one minute at -110°C to -60°C; but dinitration at 0°C is somewhat slower, requiring about 30 min for completion. Although our results show that NTFS nitration rates are not as fast in an inert solvent as they are in nitric acid/oleum systems, NTFS is a very strong nitrating system and one of the few that will convert toluene to DNT at 0°C.

NTFS shows a high degree of positional selectivity as a reagent for aromatic nitration. As with all other nitrating systems the amount of meta isomer produced in toluene nitration depends directly on reaction temperature. At -60°, -90°, and -110°C its reaction with toluene gives MNT that contains 0.53%, 0.36%, and 0.23% m-MNT, respectively. The last value is the lowest that has been reliably recorded for an MNT synthesis. Since most meta substitution takes place in the mononitration stage, the final meta isomer content in DNT can be greatly influenced by running the mononitration step at low temperatures followed by dinitration at 0-25°C. Thus, when mononitration was carried out at -110°, -90°, -60°, -30°, 0°, and 25°C, followed by dinitration at 0° or 25°C, the resulting DNT products contained 0.33%, 0.51%, 0.75%, 1.08%, 1.33%, and 1.72% meta isomers, respectively. The 0.33% value is the lowest that has been reliably recorded for meta isomers in a DNT synthesis.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

Nitration of Dinitrotoluene

The use of anhydrous mixed acid systems for low temperature dinitration of toluene led us to choose the same type of system for trinitration since in a plant operation no essential change of nitration system would be necessary.

Work on the trinitration step began with consideration of the appropriate concentration of oleum to be used and methods of ensuring reproducible reaction conditions. The choice of the SO_3 concentration determines the concentration of NO_2HSO_4, and at least two factors favor a high concentration of the nitrating agent for a manufacturing process: (1) the reaction rate, and thus the overall plant production rate, is a function of the NO_2HSO_4 concentration and (2) the reactor volume and number of reactors required to produce TNT at a specified rate are determined in part by the concentration of the nitrating agent. These factors must be weighed against safety considerations because we

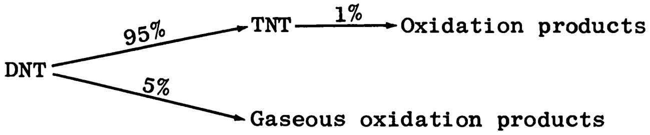
Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

have found that too high a concentration of reactants sometimes leads to runaway reactions.

High concentrations of SO_3 in sulfuric acid were deleterious to control of nitration although high concentrations of nitrating agent were possible. Rapid decomposition of starting material resulted from heat produced by trinitration with nitric acid in 65% and 40% oleum. Equimolar amounts of HNO_3 and SO_3 in 30% oleum produced a maximum temperature of 130°C and resulted in a 94.0% yield of TNT. When SO_3 in 10% excess was used to prepare the NO_2HSO_4, the temperature reached 97°C and the yield of TNT was 95.0%.

To test more carefully the effect of the SO_3/HNO_3 ratio on the yield of TNT, it was necessary to eliminate temperature as a variable. The mixed acid solution was heated in an oil bath at 90°C, and DNT was added in small portions so that the reaction mixture was maintained at 91-92°C by the heat of reaction. Essentially no effect was seen as the SO_3/HNO_3 ratio was varied in the range from 0.9 to 1.0 to 1.1; yields of 94% were obtained.

An investigation into the nature of the side reactions that limit the TNT yield to about 94% indicated that DNT undergoes competitive nitration and oxidation reactions in accordance with the following scheme:



Sulfonation was eliminated as a possible side reaction by an experiment in which DNT was treated with 15% fuming H_2SO_4 at 90°C; 99% DNT was recovered.

Trinitrobenzoic acid was established as one of the by-products of TNT oxidation. Although present in minor amounts, it was obtained as the principal constituent of at least five compounds isolated. To determine whether the major loss was due to oxidation of DNT or TNT, we tested the stability of TNT to the nitration conditions; 98.6% TNT was recovered.

Infrared analysis of samples of the gas phase over a trinitration reaction confirmed the presence of gaseous by-products; strong infrared bands for CO_2, CO, and N_2O were observed. Since no more than 1.4% of the TNT undergoes oxidative decomposition, and since some of the TNT by-products are (at least partly) solids, the major proportion of the gaseous by-products must arise from oxidation of DNT and account for about 5% of the material balance. It is obvious that the major source of loss is by oxidation of DNT.

To optimize trinitration under useable conditions, we chose 1 hr as the maximum time for completion of the reaction. We chose also to initiate the reaction at higher temperatures to avoid an exotherm that occurs when heating from ambient to the desired nitration temperature. The reaction times required for complete reaction, when the ratio of reagents was 3 moles of NO_2HSO_4 (prepared from HNO_3 and 30% oleum) per mole of DNT, were 140 min at 70°C, 100 min at 80°C, and 50 min at 90°C. The reaction could be completed within 60 min by heating for 30 min at 70°C, followed by 15 min each at 80° and 90°C. Initiating the reaction at 70°C, where the rate is much slower than at 90°C, makes it easier to control the temperature; the elevated temperatures are then used to complete the reaction after much of the initial DNT charge has been consumed.

Although the trinitration of DNT could be conducted in high yield and oxidation products were primarily gases, the corresponding inorganic reduction by-product was nitrosyl sulfuric acid. The presence of $NOHSO_4$ meant that the nitrating medium would require clean-up at some stage in the recycle of spent acids, although in nine consecutive nitrations of toluene to TNT with refortified used acid, little effect by its presence was observed. Consequently, several attempts were made to prevent DNT oxidation by (a) using oxidation inhibitors, (b) increasing the concentration of NO_2HSO_4 while lowering the reaction temperature, (c) increasing the SO_3 concentration, and (d) temperature programming the optimum nitration concentrations. An extensive study of the last procedure showed that nitration of DNT at 40°C proceeds at an appreciable rate and is accompanied by oxidation of the DNT to gaseous products. Higher temperatures, either programmed from 40° to 90°C or isothermally at 90°C, cause only a variation in nitration rates and little variation in oxidation rates.* Reactions at the higher temperatures also produce tetranitromethane (TNM) as well as CO, CO_2, N_2O, and NO_2. Comparative nitration experiments of all the DNT isomers except 3,5-DNT show rates from fastest to slowest in the order 2,6- > 3,4- > 2,4- $\cong$ 2,5- $\cong$ 2,3-DNT; all isomers undergo oxidation.

---

* A detailed kinetic study of nitration/oxidation of three DNT isomers, by D. S. Ross and N. Kirshen, is described elsewhere in this symposium.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

The nitration of 3,4-DNT at a rate faster than 2,4-DNT is unexpected and cannot be explained solely by directive effect considerations proposed by other workers (7). Introduction of an entering group on the toluene nucleus is affected not only by the orientation of the methyl and nitro groups already present but also by steric, temperature, and concentration factors. In the three meta isomers studied, two nitro groups are adjacent. One group is out of the plane of the ring and thus exerts little directing effect toward nitration. For example, in 2,3-DNT the 2-nitro group is most probably out of plane, leaving the methyl and 3-nitro groups opposing each other in directing further nitration. Conversely, in 2,4-DNT both nitro groups are in plane with the ring and thus exert deactivating effects. The methyl and 2-nitro groups direct nitration to the 4- and 6- positions; however, in 2,5-DNT these effects are counteracted by the 5-nitro group, which directs nitration to the 3-position.

The faster nitration rate shown by 3,4-DNT indicates that the 3-nitro group of 3,4-DNT is the one most probably out of plane, leaving the methyl and 4-nitro groups to direct nitration. Because the out-of-plane configuration makes 3,4-DNT similar to that of p-nitrotoluene, its nitration rate is faster than that of the other DNT meta isomers, as well as 2,4-DNT. This postulation is in line with the results obtained from our study on the nitration rates of 2,4- and 2,6-DNT.

Because the probability of a nitro group being out of plane is greater in 2,6-DNT and because its 4-position is less sterically hindered, this isomer should nitrate faster than 2,4-DNT, as shown by our results.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

TNT Isolation

The requirement for a process adaptable to plant operation made product isolation very critical. Because of the high acid strength and solubility of TNT in the acid medium, efficient crystallization of TNT at lower temperatures was necessary for recycle of the spent acids. In a typical trinitration reaction with pure 2,4-DNT, the product TNT was filtered from the nitration medium at 0°C, and again at -10°C. About 79% of the TNT produced in the reaction crystallized from solution. The composition of the wet product was 70% TNT and 30% acid. After washing and drying, this TNT had a set point of 80.6°C, showing that the isolation and purification technique gives a pure product when 2,4-DNT is used as starting material.

The amount of acid occluded by the crystals was substantially influenced by the size of the crystals. A slow rate of crystal growth, beginning while the solution was still quite warm, gave large crystals; the occluded acid amounted to about 30% to 35% of the total weight of the wet crystals or about 43% to 54% of the dry weight of the TNT. On the other hand, if extensive oiling occurred as the TNT solution cooled, very rapid crystallization took place, giving small crystals that were very difficult to filter and occluded a large amount of acid. In one such case, the acid amounted to 53% of the total weight of the wet crystals.

In trinitration of mixed DNT isomers typical of actual conditions, less than 79% of the TNT crystallizes out of the mixed acids. A value of 70% is more nearly representative of actual conditions. The remainder is recycled through the process with the acid filtrate.

Scale-up to Miniplant

A miniplant was constructed following the schematic diagram of Figure 2 that had a capacity of 2 pounds per hour when operated in a continuous mode. The principal steps, however, were most emphasized in primarily an exploratory batch study.

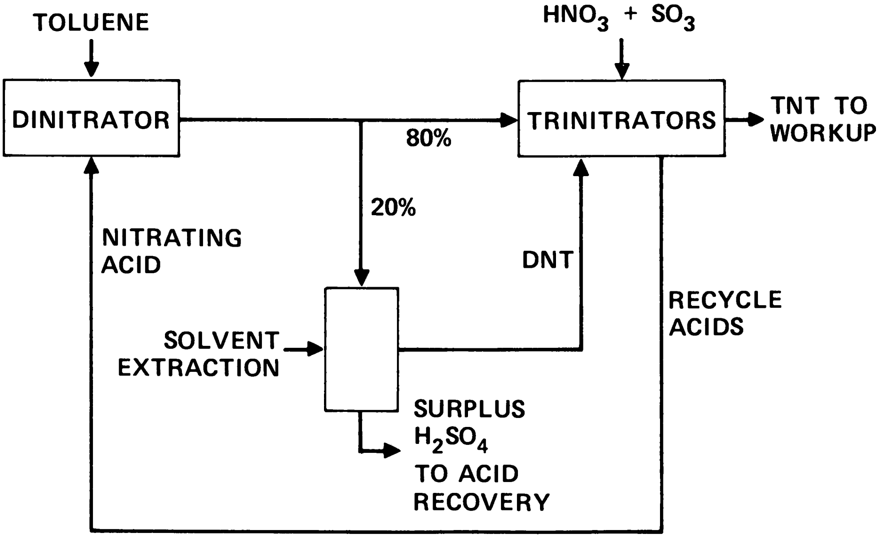


Figure 2. Process based on $HNO_3/SO_3/H_2SO_4$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

Toluene and recycled mother liquor from the trinitration step were precooled to about -10°C and allowed to react at that temperature in a strongly agitated, well-cooled, multistage turbo-reactor intended to operate in plug flow mode with toluene apportioned equally among the several stages. The toluene was rapidly dinitrated by a stoichiometric amount of NO_2HSO_4 with concurrent formation of H_2SO_4, the principal by-product of the process. Thus, the effluent from the dinitrator is a mixture of DNT and recycled TNT dissolved in H_2SO_4. The yields and conditions of the laboratory study were essentially confirmed; DNT was obtained in 97% to 98% yields with meta isomer content of 2.2 to 2.3%.

Part of the effluent was allowed to flow directly to an acid fortification tank, where fresh SO_3 and HNO_3 were added to bring the concentration of NO_2HSO_4 to the required level for the subsequent trinitration reaction. However, a portion of the dinitrator effluent was first diverted and the by-product H_2SO_4 separated by methylene chloride extraction of the DNT with a Pyrex multistage counter current extraction column. Good extraction and separation of solvent were achieved. After the methylene chloride was subsequently stripped out and recycled, the extracted DNT and TNT was joined to the undiverted dinitrator effluent stream entering the acid fortification tank.

From the acid fortification tank, the dinitration products and the fortified acids flowed in succession through three stirred trinitration reactors maintained at about 80°, 85°, and 90°C. The overflow from the third trinitrator consisted essentially of TNT dissolved in acids. The TNT was crystallized by cooling the liquors in a three-stage upflow, inclined scraped pipe crystallizer, and then filtered and dropped into a receiver containing 70% H_2SO_4, which served as the first wash for the TNT product.

In general, the chemical performance data were comparable to the laboratory results. For example, the overall TNT yield from one cycle of dinitration plus trinitration was 91.1% based on toluene and 74.3% based on nitric acid. These values may be compared with the average laboratory values of 93% and 75%, respectively.

Summary

Methods were developed for the improved synthesis of TNT to alleviate pollution problems associated with current manufacturing processes. A comparison of many nitration methods showed that modified oleum-nitric acid mixtures were the most effective at

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

giving high yields of TNT while emitting little or no atmospheric pollutants. Conducting toluene dinitration at low temperature (-10°C) eliminates oxidation and reduces the amount of the undesirable meta isomers formed to 1-2% in contrast to ca. 4% in conventional processes. Consequently, "red water" problems associated with TNT purification by treating crude product with sodium sulfite could be substantially diminished.

Thus, a two-stage nitration system was developed in which toluene is dinitrated in 99% yield at -10°C using an oleum-nitric acid mixture, followed by trinitration of the DNT in anhydrous nitric/sulfuric acid at 90°C in 94% yield. A procedure for the recovery and recycle of all acids was developed, and the overall process was confirmed in a miniplant scale-up. Other research has shown that DNT can be prepared rapidly and in high yield using anhydrous nitrate salt/sulfuric acid or nitric/sulfuric acid mixtures containing 0-7 wt% water. Meta isomer percentages are less than 2% when reaction temperatures are -10°C or lower. A unique nitrating system was also developed consisting of trifluoromethanesulfonic acid and nitric acid in an organic solvent at -110° to 30°C. This system produced mono or dinitrotoluene in high yields and with less than 0.5% meta isomer content.

Acknowledgment

The authors sincerely appreciate the support given us by the Picatinny Arsenal and Army Materiel Command and particularly the valuable contributions and continued encouragement provided throughout this study by many individuals of these organizations.

Appendix

EXPERIMENTAL PROCEDURES

General

Elemental analyses were determined by the Stanford University Microanalytical Laboratory. Infrared spectra were run on a Perkin-Elmer 237 spectrophotometer and Raman spectra on a Specs Ramalog 1401 Double Monochromator, Coherent Radiation Model 52, Mixed Gas Argon Krypton Laser. Gc analyses were run on an Aerograph 1520 gas chromatograph equipped with a flame ionization detector. Mononitrotoluene mixtures were analyzed on a 12 ft x 0.125 in., 4% QF-1 on 100/120 mesh Chromosorb G, acid-washed, DMCS-treated column. Dinitrotoluene and nitrobenzotrifluoride

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

mixtures were analyzed on a 12 ft x 0.125 in. column packed with 4% poly-m-phenyl ether (six ring) on 80/100 mesh Chromosorb G, acid-washed, DMCS-treated. Baseline separation of all DNT isomers was obtained except for the 2,3 and 2,5 isomers, which had the same retention time. A 10 ft x 0.125 in. 25% silicone oil on 100/120 mesh Chromosorb G, acid-washed, DMCS-treated column gave complete baseline separation of the six TNT isomers. Each analysis was compared with that of a standard that contained approximately the same isomer distribution.

Starting Materials

Commercial grade toluene was distilled before use to obtain fractions that were pure by gc analysis. Trifluoromethanesulfonic acid, obtained from The 3M Company under the name of trimsylate acid (FC-24), was analyzed as 99% pure by preparation of its aniline salt and was used without further purification.

Dinitration of Toluene with Nitric Acid in Oleum

The following procedure is representative of the method used to determine general reaction rates and to study the effect of temperature on the dinitration of toluene in oleum/HNO_3 mixtures.

Absolute HNO_3 (16.2 g, 257 mmole) was added dropwise to 93.5 g (ca. 50 ml) of 20.6% oleum (240 mmole of SO_3) using external cooling to maintain a temperature of 20° to 30°C. The solution was prepared in a 100-ml three-necked round-bottom flask fitted with a mechanical stirrer, thermometer, and pressure-equalizing dropping funnel with drying tube attached. The dropping funnel was then replaced with a second one containing 11.3 g of neat toluene. The NO_2HSO_4 solution was cooled in a salt-ice bath, and toluene (11.2 g, 122 mmole) was added slowly over 45 min at -6° to -9°C. After an additional 15 min, the solution was quenched in 325 g of ice. The product was extracted with methylene chloride, washed with saturated NaCl solution, dried over $MgSO_4$, and evaporated to dryness with a rotary evaporator. The solid was dried to constant weight under vacuum over KOH pellets; 22.1 g (99.4%) of DNT was obtained. This product was analyzed by gc and found to contain 15.6% 2,6-DNT, 0.6% 2,3-DNT and 2,5-DNT, 82.6% 2,4-DNT, and 1.2% 3,4-DNT.

Dinitration of Toluene with Sodium Nitrate in Fuming Sulfuric Acid

A preliminary experiment established the solubility of $NaNO_3$ in 15% fuming H_2SO_4 as 0.176 g/ml at ambient temperature. Dry

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

$NaNO_3$ (10.74 g, 127 mmole) was placed in a 100-ml flask equipped with a mechanical stirrer, thermometer, and graduated addition funnel with a drying tube attached. The system was flushed with dry nitrogen and 61 ml of 15% fuming H_2SO_4 (217 mmole of SO_3) was added from the funnel, keeping the mixture at 0°C by external cooling. After the $NaNO_3$ had dissolved, the solution was cooled to -15°C and toluene (2.80 g, 30.4 mmole) was added dropwise with vigorous stirring over 1 hr while keeping the temperature below -10°C. After 15 min the solution was poured into 300 g of ice and the product extracted with methylene chloride. The extract was dried over $CaCl_2$ and the solvent removed with a rotary evaporator; 4.88 g (88.3%) of DNT was obtained.

Dinitration of Toluene with Potassium Nitrate in Fuming Sulfuric Acid

The solubility of KNO_3 in 15% fuming H_2SO_4 was determined as 0.317 g/ml. Dry KNO_3 (7.30 g, 72.2 mmole) was dissolved in 23 ml of 15% fuming H_2SO_4 (81.9 mmole of SO_3) as above. Toluene (2.11 g, 22.9 mmole) was added dropwise at -10°C over 15 min. After an additional 15 min, the reaction mixture was quenched in 300 g of ice and worked up as above; 4.05 g (97.2%) of DNT was obtained.

Preparation of DNT with Mixed Aqueous Acids

A nitrating mixture was prepared from 280 g 96% H_2SO_4 and 27 g 70% HNO_3 (0.300 mole) to give a clear, colorless solution containing by weight 87.56% H_2SO_4, 6.16% HNO_3, and 6.29% H_2O. To the slurry that results when this solution is cooled to -35°C there was added 13.10 g of toluene (0.142 mole) over 20 min. The mixture was then stirred at -35°C for 1 hour and finally quenched by pouring onto 250 g of ice. The product was separated by extraction with seven 25-ml portions of methylene chloride. These were combined, dried ($MgSO_4$), and the solvent removed under vacuum to give 25.73 g of DNT (99.5% yield). Gc analysis of this product showed that it contained 11.13% 2,6-DNT, 0.30% 2,3- and 2,5-DNT, 87.45% 2,4-DNT, and 1.12% 3,4-DNT. Total meta isomers were 1.43%.

Preparation of MNT with Nitronium Trifluoromethanesulfonate

A solution containing 6 g (40 mmol) of trifluoromethanesulfonic acid dissolved in 100 ml of CH_2Cl_2 was placed in a 200-ml flask equipped with a mechanical stirrer, addition funnel, and thermometer. A 1.26-g sample (20 mmol) of anhydrous HNO_3 was added to this solution, causing a white, crystalline solid to separate from solution. The temperature of the mixture was lowered to -60°C by a dry ice-acetone bath, and 0.46 g (5 mmol) of toluene was added in one portion. The mixture was stirred at -60°C for 1 hr and then quickly poured onto 100 g of crushed ice. The resulting mixture was extracted with three 100-ml portions of CH_2Cl_2. These were combined and dried ($MgSO_4$), and the solvent was removed under vacuum, leaving 0.69 g (100%) of mononitrotoluenes. A gc analysis of this product showed that it contained 62.12% o-nitrotoluene, 0.53% m-nitrotoluene, and 37.35% p-nitrotoluene; a trace (< 0.1%) of dinitrotoluene was present.

Preparation of DNT with Nitronium Trifluoromethanesulfonate

Method A. A nitrating mixture consisting of 42.63 g (284 mmol) of CF_3SO_3H, 42.75 g of 96% H_2SO_4, and 7.91 g (126 mmol) of anhydrous HNO_3 was prepared in a 100-ml flask equipped with a mechanical stirrer, addition funnel, and thermometer. The solution was cooled to -24°C and 2.02 g (22 mmol) of toluene was added dropwise in 50 min. As the toluene was added, a solid product was formed and the nitrating mixture became partially frozen. Stirring was continued for 1 hr at -24° to -20°C and the reaction mixture was poured onto 1200 g of crushed ice. The resulting mixture was extracted with three 250-ml portions of CH_2Cl_2; these were combined and dried ($MgSO_4$) and the solvent was evaporated, leaving 3.83 g (97%) of a light yellow solid that was identified as a mixture of dinitrotoluene isomers by its ir spectrum and elemental analysis. Gc analysis showed that this product contained 12.20% 2,6-DNT, 0.45% 2,3- and 2,5-DNT, 86.31% 2,4-DNT, and 1.04% 3,4-DNT. Total meta-isomer content was 1.49%.

Anal. Calcd. for $C_7H_6N_2O_4$: C, 46.16; H, 3.32; N, 15.38. Found: C, 46.12; H, 3.33; N, 15.25.

Method B. A nitrating mixture consisting of 50 g (333 mmol) of CF_3SO_3H and 6.3 g (100 mmol) of anhydrous HNO_3 was prepared in a 100-ml, three-necked flask equipped with a mechanical stirrer, addition funnel, and thermometer. The mixture consisted of an insoluble complex of $2CF_3SO_3H/HNO_3$ in CF_3SO_3H. The mixture was cooled to 0°C, and 4 g (43 mmol) of toluene was added over 10 min. The reaction mixture was stirred at 0°C for 1 hr and quenched on 500 g of crushed ice. The resulting mixture was extracted with three 100-ml portions of CH_2Cl_2, which were combined and dried ($MgSO_4$). Removal of solvent left 7.75 g (98%) of a light yellow

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

solid that was identified as a mixture of dinitrotoluene isomers by ir spectrum. A gc analysis of this product showed that it contained 17.50% 2,6-DNT, 0.51% 2,3- and 2,5-DNT, 82.84% 2,4-DNT, and 0.95% 3,4-DNT.

Method C. A mixture containing 6 g (40 mmol) of trifluoromethanesulfonic acid and 100 ml of $CFCl_3$ was prepared in a 200-ml flask equipped with a mechanical stirrer, addition funnel, and thermometer. A 1.26 g sample (20 mmol) of anhydrous HNO_3 was added at 25°C, forming the $2CF_3SO_3H/HNO_3$ complex. The temperature of the reaction was lowered to 0°C, and 0.46 g (5.0 mmol) of toluene was added in one portion. The mixture was stirred for 1 hr at 0°C and poured onto 100 g of crushed ice. Three 100-ml CH_2Cl_2 extractions were combined and dried over $MgSO_4$. The solvent was removed, leaving 0.90 g (99%) of a light yellow solid that was identified as a mixture of dinitrotoluene isomers by its ir spectrum. A gc analysis of this product showed that it contained 16.47% 2,6-DNT, 0.45% 2,3- and 2,5-DNT, 82.36% 2,4-DNT, and 0.72% 3,4-DNT. Total meta-isomer content was 1.17%.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

Nitration of Dinitrotoluene with Oleum/HNO_3 Mixtures

The following procedure is representative of the method used to determine the effect of oleum and nitric acid concentrations on the preparation of TNT from DNT. It is also representative of the optimum conditions used for the preparation of TNT from DNT.

A mixture of 11.5 g (182 mmole) of absolute HNO_3 and 48.0 g of 30.3% fuming H_2SO_4 (181 mmole of SO_3) was heated to 90°C in a constant temperature oil bath. Solid 2,4-DNT (11.1 g, 61.0 mmole) was added in 0.5-g portions over 80 min; this rate of addition maintained a temperature of 91-92°C in the reaction flask. Stirring and heating of the yellow solution was continued for 1.5 hr after all the DNT had been added. Part of the TNT separated from the solution as an oil. The mixture was cooled to 25°C with an ice bath, which caused solid TNT to form, and was then poured into 140 g of ice. The product was extracted with methylene chloride, and the extract was washed with saturated NaCl solution, dried over $MgSO_4$, and evaporated with a rotary evaporator. The solid residue was dried to constant weight under vacuum over KOH pellets; 13.0 g (94.0%) of TNT was obtained. Gc analysis showed the product to be TNT.

Nitration of 2,6-DNT at 90°C in a Sealed Reactor

This general experimental procedure was used in the nitration of all DNT-isomers to study reaction rates and determine the nature

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

of gaseous by-products at 90°C. A nitrating mixture consisting of 21.60 g of 30.78% oleum (83.1 mmol of SO_3) and 5.19 g of anhydrous nitric acid (82.4 mmol) was prepared at 0° to -5°C in a 100-ml reactor. The temperature was raised to ambient and 2,6-DNT (5.03 g, 27.6 mmol) was added; DNT/HNO_3/oleum, 1/3/3. The reactor was connected to the vacuum line, cooled to -196°C, and degassed twice at less than ten microns. The reactor was sealed under vacuum, warmed from -196° to +45°C. The mixture was then heated from 50° to 90°C in 20 min and held at 90°C for a total heating time of 97 min. The break seal was ruptured and gases were collected in cooled traps during the last hour of nitration.

The gases were measured and analyzed by mass spectrometry (CO, 2652 μmol; CO_2, 4720 μmol). The trap at -78°C contained a trace of brown vapor, which was irreversibly absorbed on Porapak Q, probably NO_2. The remaining vapors in this trap were condensed into a hydrazine/ethanol solution and analyzed by uv for TNM; found 1.3 mg.

The aqueous acid was extracted with methylene chloride (3 x 75 ml), combined, washed with brine, dried ($MgSO_4$), and solvent removed at reduced pressure leaving 5.83 g of a yellow solid. Gc analysis using a 10 ft x 1/8 in. 25% Dow 500 column indicated that no residual DNT was present; 100% conversion, 92.9% yield. By consideration of the gases, TNM, and TNT formed, 97% of the DNT was accounted for.

Literature Cited

1. For good reviews of aromatic nitration, see
   (a) Hoggett, J.G., Moodie, R. B., Penton, J. R., and Scholfield, K., "Nitration Aromatic Reactivity," University Press, Cambridge, England, 1971.
   (b) Olah, G. A., and Kuhn, S. J., in "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience, New York, 1964, Chapter XLIII.
   (c) Olah, G. A., Accounts Chem. Res. (1971), 4, 240.
   (d) Ridd, J. H., Accounts Chem. Res. (1971), 4, 248.
2. Hill, M. E., and Taylor, F., Jr., J. Org. Chem. (1960), 25, 1537.
3. Coon, C. L., McDonald, G. J., and Hill, M. E., U. S. Patent 3,788,546 (1973).
4. Coon, C. L., Blucher, W. G., and Hill, M. E., J. Org. Chem. (1973), 38 (25), 4243.
5. Coon, C. L., and Hill, M. E., U. S. Patent 3,714,272 (1973).

6. Effenberger, F., and Geke, J., Synthesis, 1975, 40.
7. Holahan, F. S., Castorina, T. C., Autera, J. R., and Helf, S., J. Amer. Chem. Soc. (1962), 84, 756.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch017

18

A Low-Temperature Process for TNT Manufacture Part 2. Pilot Plant Development

W. R. HAAS, E. G. FOCHTMAN, and L. CICIORA
IIT Research Institute, 10 West 35th Street, Chicago, Ill. 06016

D. YEE
Picatinny Arsenal, Dover, N.J. 07801

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

The disposal of red water and of pink water from the manufacture of TNT has been a problem for several decades. The current emphasis on the minimizing of the environmental impact from government operations made it necessary to re-examine the entire process with a view to reducing this very difficult water pollution problem. With this goal in mind, Picatinny Arsenal contracted with the Stanford Research Institute (SRI) to investigate new processes for the manufacture of TNT. The SRI work resulted in the successful laboratory demonstration of a process which minimizes the formation of the meta isomer of toluene, the prime cause of pollution. This process was partially demonstrated in a 2 lb TNT/hr mini pilot plant. The scale of this plant was such that a number of difficulties were encountered; however, there was no indication that their laboratory work would not be substantiated if a larger plant were constructed.

The basic feature of the SRI process involves low-temperature (-10°C) nitration, to the dinitrate of toluene, followed by a higher temperature (90°C) trinitration. The nitrobody concentration is maintained below the solubility limit in the nitration acid which results in the process being conducted in a single phase mixture.

Process Description

The low-temperature TNT process was developed at SRI for Picatinny Arsenal. Modifications to the standard process include:

- co-current flow of single phase anhydrous acid and the nitrobodies
- low-temperature (-10°C) dinitration
- crystallization and filtration of the product TNT from the anhydrous acid

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

The process flow diagram for the pilot plant is shown in Figure 1. The design incorporates the process as defined by SRI and system changes that were recommended by Picatinny Arsenal personnel.

Dinitration, the first major step in the process, takes place by mixing the toluene with recycle acid at -8°C. After reacting, this mixture flows through a flow splitter that divides the stream into two equal parts. One portion is sent directly to the trinitration reactors and the other to a water dilution tank where the nitrobodies separate from the acid phase and are sent to the trinitrators. The acid phase is purged from the system.

A mixture of 60% oleum and nitric acid is used for the trinitration. The temperature of this exothermic trinitration reaction is controlled at or below 90°C to prevent excessive oxidation. The reaction requires approximately one hour.

The mixture of TNT dissolved in nitration acid leaving the trinitrators is fed to a crystallizer system where the temperature is lowered by removing the heat through the vessel walls. This system consists of five stirred tank crystallizers in series with each operating at successively lower temperatures. The crystallizer effluent contains about 16.5 wt% total TNT at -5°C.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Dinitration

The initial reaction step in the low-temperature TNT process results in the conversion of toluene to dinitrotoluene (DNT). The major changes from the existing process occur in this portion of the operation; therefore, extensive pilot plant data will be needed.

The dinitration reaction is conducted in an anhydrous H_2SO_4 medium near the freezing point of the entire mixture (i.e., ∿10°C). The over-all reaction can be written:

$$CH_3\text{-}C_6H_5 + 2NO_2HSO_4 \xrightarrow[-10^\circ C]{H_2SO_4} CH_3\text{-}C_6H_3(NO_2)_2 + 2H_2SO_4$$

Nitronium bisulfate, NO_2HSO_4, is the nitrating agent which results from reacting nitric acid with the sulfur trioxide in oleum. It is delivered as the functional part of the recycle acid.

The dinitration chemical reaction has been shown to be nearly instantaneous and relatively independent of nitric acid concentration in the SRI laboratory work. Toluene has a very low solubility in the nitrating acid and therefore the mononitration reaction is highly dependent on mass transfer of the reactants. This fact was taken into account in the pilot plant design by using a recycle reactor system with the toluene added just ahead of the centrifugal circulating pump. This system will atomize the toluene in the nitration acid stream to facilitate mass transfer.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

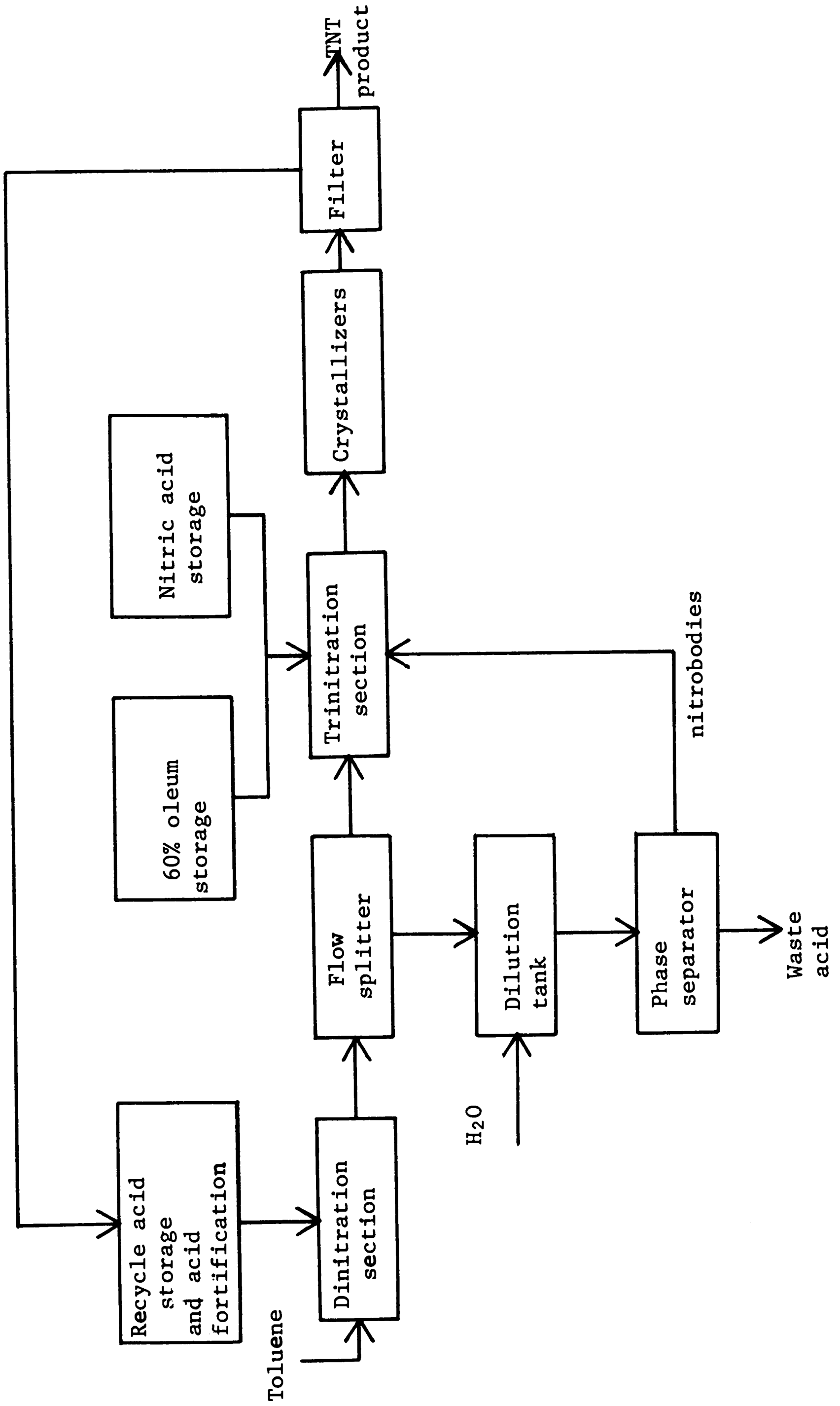


Figure 1. *Diagram of low temperature TNT process*

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

The dinitrator recycle reactor is shown schematically in Figure 2.

The SRI laboratory work showed that lowering the temperature from 33°C to -8°C in the dinitration step resulted in reducing meta isomer concentration in the product from 2.4% to 1.8%. The recycle reactor concept was incorporated in the dinitrator design to insure that the design temperature was maintained.

The heat of reaction was calculated to be -1819.5 Btu/lb toluene by SRI and measured at -1410 Btu/lb toluene at Picatinny. Based on the SRI laboratory yield information, 22 lb/hr of toluene feed will produce the process design capacity, 50 lb TNT/hr.

The dinitrator section of the pilot plant contains four (4) recycle reactors. The acid flows through the reactors in a series fashion and one-third of the toluene is added to each of the first three reactors with the fourth as an additional safety factor to assure complete reaction.

The sensible heat capacity of the reaction mixture with a 0.5°C temperature rise will absorb the heat of reaction at a recycle flow rate of less than 100 gpm. This heat is removed in a 60 ft^2 heat exchanger with a 7°C driving force.

Dinitrator Design Summary

The dinitration of toluene is conducted in four specially designed recycle reactors. The acid stream moves through the reactors in series and toluene is added to each of the first three.

The basic reasons for this pilot reactor design are:

- to insure close control of the exothermic reaction
- to determine the effect of decreasing acid concentration on the reaction

The temperature range of the reaction mixture in this system is controlled by the recycle flow rate. These recycle reactors will assure adequate contact of the two-phase reaction mixtures with an insignificant temperature rise of less than 0.5°C when the recycle rate is 100 gpm or greater. The temperature of the process fluid at the heat exchanger outlet can be controlled by automatically adjusting the coolant flow rate.

The dinitration reactor system is designed to deplete the nitration capability of the acid phase. Experimental work has shown that a colored complex forms if insufficient nitric acid is present. Some pilot plant data should be developed to determine if the effect will be important in this system and if the reaction rate will be affected by the low nitration capacity of the acid.

Since toluene is added at three discrete points in the reactor system and the stream can be sampled after each addition, the extent of reaction and the nature of the product can be

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

TR - Temperature Recorder
FR - Flow Recorder
FRC - Flow Recorder Controller
S - Sample Point

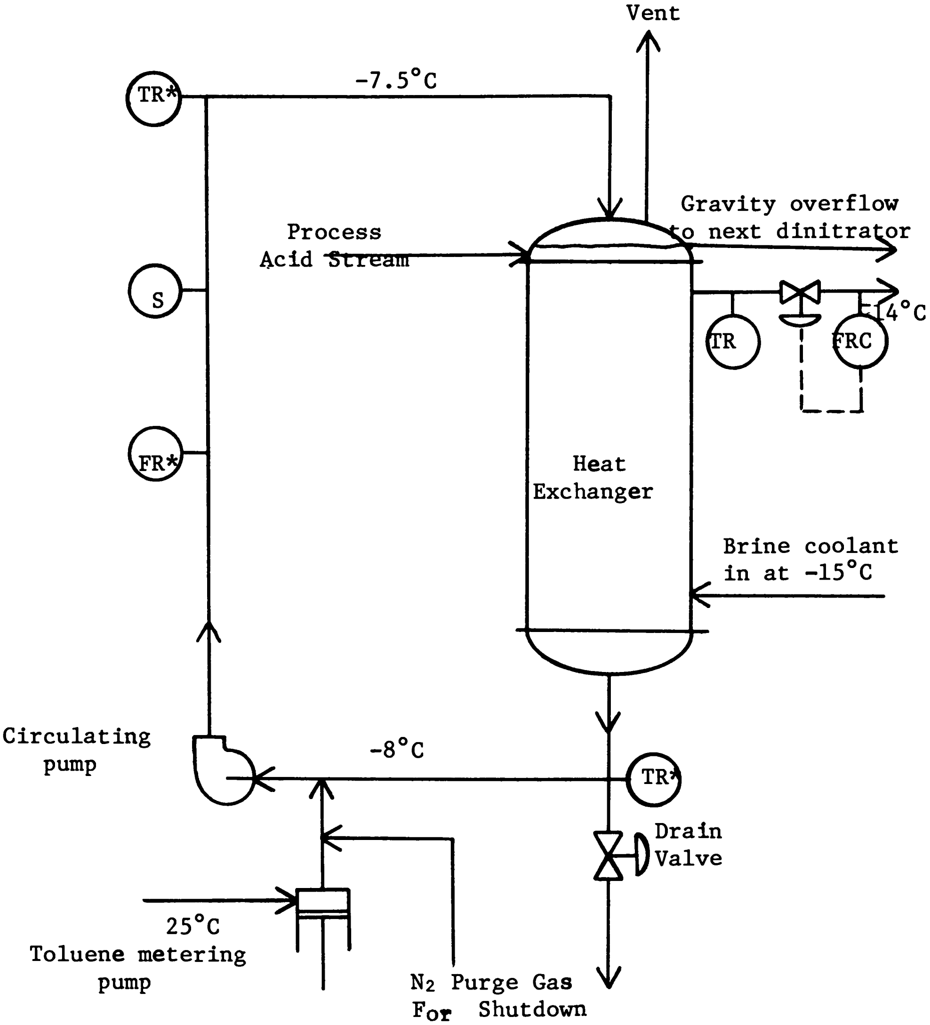


Figure 2. Dinitrator recycle reactor

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

determined at each point. A fourth reactor with no toluene feed is included to assure adequate holding time if the reaction rate is reduced and to increase the capacity of this portion of the pilot plant if it is necessary when operating the subsequent units.

Flow Splitter. The dinitrator effluent is a solution of TNT, DNT, and oxidation products dissolved in by-product sulfuric acid. The effluent stream is heated from -8°C to 35°C and divided at this point in the process by flowing into a tank from which a predetermined flow of the product is pumped to the trinitrator while the remainder overflows to the nitrobody (nitrated organics) recovery system. Approximately 220 Btu/lb TNT produced must be added to the flow splitter. In the nitrobody recovery system, the TNT and DNT are recovered and the sulfuric acid is exhausted from the process.

The fraction of acid directed to the nitrobody recovery system under steady operation is determined by the concentration of SO_3 and HNO_3 in the acid feed system. When 60% oleum and 100% HNO_3 are fed to the process, the flow splitter should operate with 50% of the dinitrator effluent flowing to the trinitrators while the remainder is exhausted through the nitrobody recovery system.

Nitrobody Recovery. Approximately 50% of the nitrobodies in the dinitrator effluent leave the flow splitter with the waste acid. SRI used a liquid-liquid extraction unit with methylene chloride as a solvent followed by distillation to reclaim these organics. Due to the corrosive nature of the acid phase after it had contacted the methylene chloride, a different separation method has been devised with assistance from Picatinny Arsenal.

The waste acid stream from the flow splitter flows to a dilution tank where it is diluted to 70% acid with water. Approximately 520 Btu/lb TNT produced must be removed from this operation. The nitrobody solubility is lowered to 1 wt%. Twenty-nine lb/hr of nitrobodies will separate at this point and be sent to the trinitrator.

When water is added to the dinitration acid effluent, nitrosylsulfuric acid ($NOHSO_4$), an oxidation product, begins to decompose into H_2SO_4 and NO_x gas. This gaseous effluent must be trapped and scrubbed to minimize air pollution.

DNT Reactor Product. The DNT reactor is designed to operate at -8°C with anhydrous recycle acid. Laboratory data obtained at SRI indicates that at steady state conditions the dinitrator product will contain some TNT and $NOHSO_4$ that enters the dinitrator in the recycle acid. The dinitrator effluent composition expected from this pilot design is shown in Table 1.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Table I

COMPOSITION AND AMOUNT OF DINITRATOR EFFLUENT
FOR 50 lb/hr TNT PRODUCTION

Compound	Rate, lb/hr	Wt %
DNT	46.70	12.5
TNT	20.40	5.5
HNO_3	0.61	0.2
H_2SO_4	256.56	68.9
$NOHSO_4$	47.66	12.8
HNO_2	0.37	0.1
	372.30	100.0

Acid Fortification System. The nitric acid and oleum needed to trinitrate toluene is mixed with sulfuric acid in an independent loop. The TNT yield and quality is dependent on the amount of and the ratio of these materials; thus, this feed system must be well controlled.

In the proposed SRI process, sulfur trioxide, sulfuric acid, and nitric acid were added to the portion of the dinitrator effluent that flows to the trinitrator. This concept has been changed to avoid some of the safety hazards they encountered with TNT precipitation in the fortification tank and to utilize 60% oleum in place of pure SO_3 which should improve the process economics by reducing existing plant auxiliary equipment changes.

The 60% oleum and nitric acid are fed to a recycled loop that contains a centrifugal pump and a heat exchanger to control the temperature. The weight ratio of HNO_3 to 60% oleum will be controlled at 1 to 2.48 and that mixture will be added to the first trinitrator at a weight ratio of 9.35 to 1 based on toluene feed. Approximately 4.12 lb of mixed acid/lb TNT produced is needed for the reaction.

Mixing of SO_3 and HNO_3 in a sulfuric acid solvent is exothermic. The following reaction occurs:

$$SO_3 + HNO_3 \rightarrow NO_2HSO_4$$

and produces heat at the rate of 743.4 Btu/lb HNO_3.

The reaction is nearly instantaneous so, to avoid hot spots and promote mixing, the feeds enter a stream of mixed acid recycling at a large enough rate so the sensible heat of a 5°C rise in temperature (60-65°C) will absorb the heat of reaction. This energy is removed with a water cooled heat exchanger in the recycled loop.

The reactor feed acid is removed from the loop at 4.09 lb/lb TNT produced; the composition is given in Table II. This feed is added to the first trinitrator.

Table II

COMPOSITION AND FLOW RATE OF TRINITRATOR MIXED ACID FEEDS

Material	Rate, lb/lb TNT produced	Wt %
H_2SO_4	1.173	28.7
SO_3	1.76	43.0
HNO_3	1.16	28.4
	4.093	100.1

Trinitration Reactor System

The reaction between dinitrotoluene and nitronium bisulfate is

$$CH_3\text{-}C_6H_3(NO_2)_2 + NO_2HSO_4 \xrightarrow[H_2SO_4]{90^\circ C} CH_3\text{-}C_6H_2(NO_2)_3 + H_2SO_4$$

and proceeds rather slowly.

SRI has shown that little or no product change occurs when the nitrobody concentration is low enough to maintain a single phase in the reactors as compared to the present system where a two-phase mixture exists. The reactor concept is simplified and made safer using this approach because the separators between vessels are eliminated and the mixing power requirement needed to maintain the pure nitrobody phase dispersed is reduced.

The following feed material is added at a continuous rate to the trinitrator system to produce 50 lb/hr of TNT:

205 lb/hr of mixed acid

189 lb/hr of dinitrator effluent

29 lb/hr of dinitrator effluent nitrobodies

The trinitration reaction rate showed a DNT concentration dependency in batch reaction run by SRI with similar mixtures. At 90°C, complete reaction of DNT was observed in about 1 hour. The heat of reaction was measured at 455.4 Btu/lb DNT in these experiments. Therefore, 394.3 Btu/lb TNT produced will be generated in the pilot trinitrators.

The experimental work done at SRI showed that the trinitration reaction rate is insignificant at temperatures below 60°C and when the temperature is greater than 90°C excess oxidation occurs. The oxidation reactions did not appear to selectively destroy unsymmetrical TNT isomers using the conditions tested.

The pilot plant was designed to use three 30-gal jacketed stirred tanks in series with 21 ft^2 of heat exchange for each provided by a combination of the jacket and internal coils. This

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

system operating at 90°C should provide for adequate time to completely convert the nitrobodies to TNT.

The expected product solution is shown in Table III.

Table III

COMPOSITION AND FLOW RATE OF TRINITRATOR EFFLUENT

Compound	Flow, lb/lb TNT produced	Wt %
TNT	1.397	16.52
HNO_3	0.649	7.68
SO_3	0.799	9.45
H_2SO_4	4.593	54.32
$NOHSO_4$	1.016	12.02
	8.454	99.99

Crystallization

The pre-pilot plant crystallizer used by SRI consisted of an inclined, jacketed, upflow, scraped-pipe crystallizer. That section was followed by a cylindrical, porous, stainless steel filter. A hollow, Teflon-coated screw extended through the entire length and was used to move the TNT solids out the top of the device. The SRI researchers encountered problems due to filter and feed line blockages. They improved the operating conditions by diluting the feed with filtrate. This did not appear to lend itself to either the pilot facility or production equipment because it shifts the heat load toward the cooled end of the crystallizer equipment. The driving force for heat transfer has to remain small there to avoid freezing the acid solvent on the exchanger surface; therefore, the surface area will have to be uneconomically large.

Additional laboratory data were obtained at Picatinny Arsenal and used to develop the following specifications for a stirred tanks in series crystallizer system. The following criteria were developed from that data.

- A stream containing approximately 16.5 wt% TNT can be used as crystallizer feed without becoming too viscous to flow at crystallizer operating temperatures.
- A final crystallizer temperature of -5°C is sufficient to recover the product TNT crystals.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

- A minimum coolant temperature of -15°C can be used to cool the last crystallizer without freezing the process stream.
- Five crystallizers can be incorporated to help cool the product stream. (This gives a gradual temperature progression resulting in larger TNT crystals).
- A phase separator may be needed after a trinitration holding tank (80°C) to collect any organic that may not be in solution. Reportedly, crystallization of a two-phase system results in solid TNT lumps and small crystal size.

Effect of Temperature on Crystallization. The solubility of TNT in a synthetic trinitrator acid at different temperatures was determined by Picatinny Arsenal. The data are given in Table IV.

The information presented in the SRI report indicated a high degree of supersaturation existed in the crystallizer used in their studies. This occurs when the crystallization rate is slow compared to the temperature change. The stirred tanks in series crystallization process suggested for the pilot plant is less affected by the slow rate of crystallization because large holding times are available at each specified temperature in the system.

The major heat transfer between the warm stream entering a crystallizer vessel in this system and the bulk fluid will be due to intimate mixing. This mixing will make the crystallizer volume more homogeneous and eliminate local volumes containing highly supersaturated fluid which promotes TNT crystal nucleation and thus small crystals.

Pilot Crystallizer

The pilot plant crystallization system design is shown in Figure 3. Direct feed of the trinitration effluent into the crystallizers with no recycle of cold dilute filtrate is believed a satisfactory method of operation.[1] The total heat load can be more equally distributed over the five crystallizers and eliminates the need for the high heat flux in the last vessel which results when filtrate recycle is used as a diluent.

Table V gives data on each of the crystallizers. The temperature of the coolant in each heat exchanger is critical. If the heat transfer surfaces are too cold, primary crystal

---

[1] A small stream of material from the last crystallizer is recycled to furnish seed crystals in the first vessel.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Table IV

TNT SOLUBILITY IN SYNTHETIC TRINITRATOR ACID

Synthetic Acid Composition

Compound	Wt %
H_2SO_4	75.8
SO_3	13.4
HNO_3	10.6

TNT Solubility in Acid Mixture

Temperature, °C	Dissolved Concentration, wt%
70	17.1
60	14.7
45	10.8
25	7.75
0	5.8
-10	5.3
-30	3.65

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

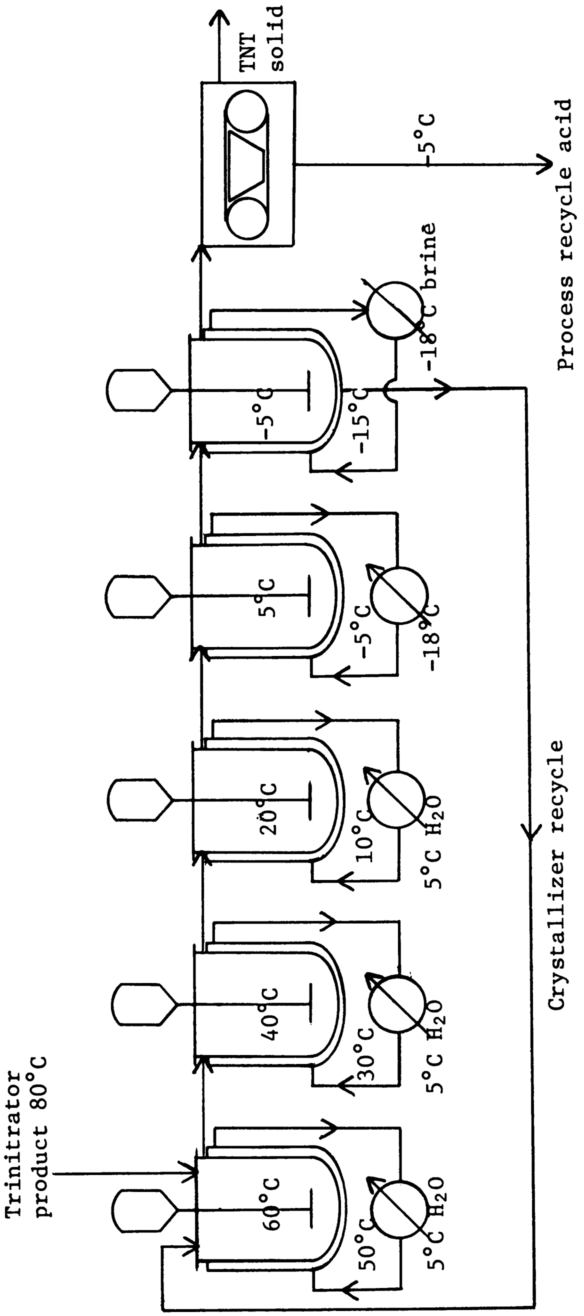


Figure 3. TNT pilot crystallizer system

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Table V

CRYSTALLIZER DATA
for 50 lb/hr TNT Production

Crystallizer	1	2	3	4	5
Operating temperature, °C	60	40	20	5	-5
Viscosity of process fluid, cp	10	50	57	125	200
Q - heat load, Btu/hr	5083	5083	5083	3812	2541
Mean coolant temperature, °C	50	30	10	-5	-15
h_i, inside film coefficient, Btu/(hr)(ft^2)(°F)	168	97.2	84.5	71.3	61.5
h_j, coolant film coefficient, Btu/(hr)(ft^2)(°F)	90	77	61	160	145
Coolant	H_2O	H_2O	H_2O	25 wt% $NaNO_3$	25 wt% $NaNO_3$
U_{OA}, over-all heat transfer coefficient, Btu/(hr)(ft^2)(°F)	55.5	41.3	34.3	47.1	41.5
Theoretical area needed, ft^2	5.1	6.84	8.2	4.5	3.4

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

nucleation occurs and results in small crystals which could block the lines connecting the vessels. Therefore, a driving force of 10°C was chosen for each crystallizer.

Filtration

A continuous filter is incorporated into the low-temperature TNT pilot plant to separate the crystalline TNT product from the acid. The equipment must be capable of removing 50 lb of 100-μm needle-shaped TNT crystals per hour from filtrate with the characteristics shown in Table VI.

Table VI

RECYCLE ACID CHARACTERISTICS

Temperature	-10°C
Viscosity	250 - 300 cp
Flow rate	0.472 gal/lb TNT produced

Material	Composition lb/TNT produced	Wt %
TNT (dissolved)	0.378	5.3
HNO_3	0.616	9.7
H_2SO_4	4.397	62.0
SO_3	0.76	10.7
$NOHSO_4$	0.953	13.4

The continuous filtration cycle is composed of the following operations:

- cake formation
- deliquoring or drying
- washing
- deliquor

Cake formation time is defined as the period of time between application of the slurry to the filter and when the cake surface is dry. The deliquoring time is the period that follows when gas is drawn through the cake to remove occluded filtrate. This period is not well defined, but should end before the cake cracks. Time must be allowed for a series of washing and drying operations with different composition wash liquors.

The Picatinny Arsenal staff conducted filtration experiments to obtain the data needed to design a continuous belt filter. The following filtration cycle was developed for the pilot process:

- cake formation
- deliquor
- 70% H_2SO_4 wash
- deliquor
- H_2O wash
- dewater

The data are shown in Table VII.

The data used to design a filter belt were:

- form time (F.T.) = 25.0 sec = 0.42 min
- form rate (F.R.) = 2.3 lb TNT/ft min
- product rate (P.R.) = 50 lb TNT/hr = 0.83 lb/min
- belt width (B.W.) = 1 ft

The belt speed, S, needed to obtain the prescribed cake thickness is:

$$S = \frac{\text{P.R.}}{(\text{F.T.})(\text{F.R.})(\text{B.W.})} \text{ ft/min}$$

$$= \frac{0.83}{(0.42)(2.3)(1)} = 0.85 \text{ ft/min}$$

The times for individual operations are:

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

Table VII

PILOT PROCESS FILTRATION CYCLE USING A 0.1-ft^2 TEST LEAF

	Experiment				
	1A	1B	2A	2B	3
Initial Filter					
Form time, sec	35	17	23	18	83
Form rate, lb/ft^2/min	2.32	2.68	3.54	2.4	1.57
Cake thickness, cm	1.3	0.7	1.4	0.9	2.0
Drain time, min	3	1.5	2	2	5
g acid/g TNT in cake	-	-	1.24	1.24	1.02
Dry cake weight, g	1.35	0.76	1.36	0.72	2.18
Vacuum, in Hg	10		20		20
70% acid wash					
Form time, sec	8	3	6	-	6
Drain time, min	1	0.5	-	-	2
TNT loss, %	-	7.6	7.2	9.0	6.1
Water wash					
Drain time, min	0.5	0.5	-	-	0.5
TNT loss, %	-	0.6	-	-	
Dry cake density	0.508	0.530	0.474	0.392	0.530

form	0.42 min
deliquor	2.00
70% H_2SO_4 wash	0.10
deliquor	1.00
H_2O wash	----
dewater	0.50
	4.02 min

The minimum active belt length is

$$0.86(4.0) = 3.44 \text{ ft}$$

A continuous belt filter should serve this purpose well. The standard design will have to be altered to operate in the explosive atmosphere and the filter unit will have to be enclosed in an environmental chamber that will control the temperature at -10°C and contain any acid fumes that may be exhausted. All pumps should be mounted outside the chamber to reduce the heat load.

Recycle Acid

The filtrate removed from the cake contains approximately 2/3 of the nitric acid and sulfur trioxide that was fed to the trinitrators. This stream is recycled back to tanks where the acid concentrations are adjusted and then it is used as feed for the dinitrators.

Product

The washed crystallized TNT cake that is removed from the belt goes to a melt tank where it is heated with water to remove occluded acid. The two-phase liquid stream is separated with the heavier oil being the TNT product and the lighter water/acid solution being a waste stream.

Instrumentation System

An electronic instrumentation system with computer compatibility was incorporated in the design to control the TNT pilot plant. All components must be Underwriters Laboratory listed intrinsically safe or suitable for Class I, Group D, Division 2 operation.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

An instrumentation panel-board is located in the remote control building. It will be laid out in a manner to follow the process with recorders, controllers, indicators and manual loaders in convenient systematic use-oriented positions.

The control equipment will permit operation of the pilot plant from the remote control building. The electrical signals leaving the control building will be directed through zener diode barriers that essentially short the field circuit when an over-voltage is detected. This will protect the process area from receiving energy from control system components that could result in a hazardous condition. The control system power in the process area will never exceed the 24 V, 20 ma level.

The control equipment located in process area will operate on the power specified above. The sensing elements will monitor pressure and temperature and linearly convert the process variable into a level of the control power. The process stream control elements will function on 3-15 psi air signals. These air signals will originate in the process building by controlling the instrument air supply pressure with an electrical signal that originates from a controller or manual loader in the control building.

All process wetted control parts will be made of 316L or 304L stainless steel or alloy 20. All external field casings will be suitable for mounting in a highly corrosive atmosphere as described below. The equipment that will be in the process streams or vessels will be fabricated from material impervious to the corrosive effects of sulfuric acid, nitric acid, and oleum. All of the above acids and acid mixtures may be present in water solutions varying in concentration from 0-100%.

Summary

A TNT pilot plant design based on laboratory information has been described. The process includes two new manufacturing technology steps, a low temperature (-8°C) dinitration reactor and a TNT crystallization unit.

This new single phase reaction technique for manufacturing TNT has possibilities of reducing air and water pollution and improving the operational safety of munition plants.

Construction of the pilot plant or a modification of the design is now under consideration by the Army.

Acknowledgement

This work was supported by Picatinny Arsenal under Contract No. DAAA21-73-C--743. The authors gratefully acknowledge their financial support and guidance furnished during the duration of the contract.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch018

19

Low Temperature Process for TNT Manufacture Part 3. Computer Simulation

R. W. HUTCHINSON and D. GOLDSTEIN

Picatinny Arsenal, Dover, N.J. 07801

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

Purpose

During the process of designing the TNT pilot plant, questions arose concerning plant start-up. The coupling of the two ends of the process by the recycle stream made it very difficult to "think through" proposed start-up schemes. It was felt that a dynamic model would be an ideal way to answer questions regarding start-up and to verify the IIT Research Institute (IITRI) design. Development of the model during the final design stage seemed well timed since the design would provide a basis for the model, while, at the same time, the model could be used to investigate design changes which, if shown to be advantageous, could be readily incorporated.

The purposes of the dynamic simulation were, therefore, to (1) verify the IITRI design and test it under start-up and normal run conditions, (2) test alternate start-up procedures in order to determine the best way to handle the recycle and crystallization operations, and (3) determine dynamics of the pilot plant in order to estimate acid sampling periods and critical sampling and control points. In addition, it was felt that the model would provide a useful format for data logging and correlation once the pilot plant was in operation. Longer-range plans included the use of the model in on-line, high-level, control strategies.

Approach

A simplistic, building-block approach was used in developing the model. For each vessel, a dynamic material balance was written. The resulting system of first-order differential equations was coupled through the common inlet and outlet streams.

Equations 1 and 2 are the general mass balances applying to all vessels, assuming perfect mixing.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

$$FI_i - R_i - FO_i = VOL\ (dC_i/dt) \tag{1}$$

$$C_i = FO_i/q \tag{2}$$

where

FI_i = inlet flow of component i, lb/hr.

R_i = reaction rate of component i, lb/hr.

FO_i = outlet flow of component i, lb/hr.

VOL = vessel volume, ft^3.

C_i = concentration of component i, lb/ft^3.

t = time, hr.

q = volumetric flow, ft^3/hr.

Then

$$dC_i/dt = d(FO_i/q)/dt = (1/q^2)(dqFO_i/dt - FO_i dq/dt) \tag{3}$$

Combining Equations 1 and 3 results in Equation 4, which when integrated for each component and each vessel gives the flow of each component from each vessel.

$$dFO_i/dt = (q/VOL)(FI_i - R_i - FO_i) + (FO_i/q)(dq/dt) \tag{4}$$

The last term in Equation 4 can be considered as a correction term to account for changing volumetric flow rates with time. In this system the term is very small, although not zero, since density changes do occur in the vessels whenever reaction takes place. The reaction rate terms, R_i, are based on kinetic data.

The dinitration of toluene appears to occur instantaneously in the anhydrous acids used in the process: Thus,

$$R_{toluene} = -R_{DNT} = FI_{toluene}$$

The rate of trinitration is much slower than that of dinitration, and a more complicated, kinetically dependent model is required. The stoichiometric equation

$$DNT + HNO_3 \xrightarrow{H_2SO_4} TNT + H_2O$$

for trinitration is represented kinetically as the bimolecular rate process:

$$\frac{d\ C_{TNT}}{dt} = k_2\ C_{HNO_3}\ C_{DNT} = R_{TNT} \tag{5}$$

where the C's are molar concentrations, moles/ft^3.

The bimolecular rate constant, k_2, is given by:

$$k_2 = k_2' \frac{C_{NO_2^+}}{C_{HNO_3}} \qquad (6)$$

where $C_{NO_2^+}$ is the molar concentration of the active nitrating species, the nitronium ion [1]. In order to utilize the above rate expression in the material balance of Equation 1, the specific molar rate, R, must be expressed as the bulk mass rate:

$$R_{TNT} = \hat{R}_{TNT}\,(MW_{TNT})\,(VOL) \qquad (7)$$

Combining Equations 5, 6 and 7 gives the rate expression:

$$R_{TNT} = k_2'\ MW_{TNT}\ VOL \left[\frac{C_{NO_2^+}}{C_{HNO_3}}\right] C_{HNO_3}\ C_{DNT} \qquad (8)$$

The influence of temperature upon reaction rate is taken into account by assuming that the constant, k_2', exhibits an Arrhenius dependence:

$$k_2' = k_{TNT} \exp\left[\frac{-E_{TNT}}{RT}\right] \qquad (9)$$

where

k_{TNT} = frequency factor (124.5 hr^{-1})*

E_{TNT} = activation energy (9300 Kcal/lb-mole)*

T = temperature (°K)

R = Universal gas constant

(*These values are based on fitting the model to data taken from the continuous TNT lines at Radford Army Ammunition Plant.)

Substitution of Equation 9 into Equation 8 gives the final expression:

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

$$R_{TNT} = k_{TNT} \exp\left[\frac{-E_{TNT}}{RT}\right] MW_{TNT}\ VOL \left[\frac{C_{NO_2^+}}{C_{HNO_3}}\right] \cdot C_{HNO_3}\ C_{DNT} \qquad (10)$$

Use of Equation 10 as a model for trinitration depends upon the ability to compute the nitronium ion concentration from the acid equilibrium reactions which occur. For the anhydrous acid mixtures used in the process, three separate acid concentration regions, each exhibiting different equilibrium, are defined.

In the first region (nitric limited), pyrosulfuric acid ($H_2S_2O_7$) is in large excess of the nitric acid to the extent that:

$$[HNO_3] \leq 0.5\ [H_2S_2O_7]$$

where [ ] indicates molar concentration, moles/ft^3.

The equilibrium expression governing acid concentrations in this region is [2]:

$$HNO_3 + 2H_2S_2O_7 \rightleftharpoons NO_2^{\ +} + HS_2O_7^- + 2H_2SO_4 \qquad (11)$$

Equation 11 is believed to go completely to the right so that in this region the equilibrium nitronium ion concentration is equal to the initial concentration of molecular nitric acid.

In the second region, the pyrosulfuric acid is only in moderate excess of the nitric acid such that:

$$0.5\ [H_2S_2O_7] < [HNO_3] \leq [H_2S_2O_7]$$

Equilibrium in this case is more involved with the following reactions influencing the final nitronium ion concentration [2]:

$$HNO_3 + 2H_2S_2O_7 \rightleftharpoons NO_2^+ + HS_2O_7^- + 2H_2SO_4 \qquad (12)$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (13)$$

$$H_3O^+ + HS_2O_7^- \rightleftharpoons 2H_2SO_4 \qquad (14)$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

$$NO_2^+ + 2HSO_4^- \rightleftharpoons HNO_3 + HS_2O_7^- \qquad (15)$$

Although Equations 12 through 15 are simultaneous, it is assumed in the model that equilibrium is reached through the following sequence: (1) an amount of HNO_3 equal to half the molar amount of $H_2S_2O_7$ present is completely converted to nitronium ions via Equation 12. (2) The remaining molecular nitric then begins dissociation via Equation 13. As the H_3O^+ is generated, it reacts immediately with the $HS_2O_7^-$ formed in Equation 12. Since there will always be more $HS_2O_7^-$ formed in Equation 12 than there will be H_3O^+ via Equation 13 and since Equation 14 is essentially irreversible, the H_3O^+ formed will continuously be removed from the system, thereby, driving Equation 13 completed to the right. NO_2^+ and HSO_4^- then recombine via Equation 15 to establish the final nitronium ion equilibrium. If the concentration of molecular nitric acid at equilibrium (after Equation 15) is given by x it can be shown that at equilibrium:

$$[HS_2O_7^-] = [H_2S_2O_7]_o - [HNO_3]_o + x$$

$$[NO_2^+] = [HNO_3]_o - x$$

$$[HSO_4^-] = 2[HNO_3]_o - [H_2S_2O_7]_o - 2x$$

where the subscript "zero" represents initial concentrations.

The mass action expression for Equation 15 is given by

$$K_{eq} = \frac{[HNO_3]\ [HS_2O_7^-]}{[NO_2^+]\ [HSO_4^-]^2} \qquad (16)$$

Substitution of the equilibrium concentrations into Equation 16 gives

$$K_{eq} = \frac{x([H_2S_2O_7]_o-[HNO_3]_o + x)}{([HNO_3]_o-x)\ (2[HNO_3]_o-[H_2S_2O_7]_o-2x)^2} \qquad (17)$$

If K_{eq} and the initial concentration of the acid components are known, x (and therefore the nitronium ion concentration) can be found by successive iteration of Equation 17. An internal halving procedure is employed for this purpose in the model, with the value of K_{eq} being set at $0.2\left[\frac{\text{lb-moles}}{\text{ft}^3}\right]^{-1}$.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

In the third oleum region (oleum limited), nitric acid exists in excess of the pyrosulfuric acid such that

$$[HNO_3] > [H_2S_2O_7] .$$

Here, the same equilibria are in effect as for the second region [2], but now the amount of $HS_2O_7^-$ formed in Equation 12 is not sufficient to remove from the system all of the H_3O^+ formed via Equation 13. Thus Equations 12, 13 and 14 act as non-equilibrium reactions only up to the point at which the $HS_2O_7^-$ formed via Equation 12 is depleted via Equation 14. Beyond this point Equations 13 and 15 act as equilibrium reactions to establish the final nitronium ion concentration. In the model, chemical element material balances are used in conjunction with an interval-halving iteration procedure to simultaneously solve Equation 16 and the mass action expression for Equation 13, thereby arriving at the equilibrium concentration of nitronium ion. The interested reader can find the details of this procedure in Reference 3.

In addition to trinitration kinetics, it was also important to develop a model for the solubility of organics in mixed acid media. Organic solubilities were determined experimentally for the acid mixtures encountered. The solubility of organics in the 70% spent acid at 55°C is 1%. The percent solubility or organics during crystallization is described by the following equation over the temperature range of 90 to -20°C:

$$\text{weight \% TNT dissolved} = 874 \quad \exp(-1460 / {}^\circ K) \qquad (18)$$

The solubility equations, the mass balance equations, and the reaction rate equations are combined to form a set of simultaneous, first order, differential equations readily solved by numerical integration. The volumetric flow rate, q, is calculated by summing the products of component flows and densities. The correction term, dq/dt, is approximated numerically as $(q_t - q_{t-\Delta t})/\Delta t$, where Δt is the time step for numerical integration.

The Euler method is used to integrate each of differential equations:

$$FO_i(t + \Delta t) = FO_i(t) + (dFO_i(t)/dt)\Delta t$$

Higher order, more accurate algorithms will be tested in the future. However, for this system the Euler equation gives satisfactory results using a CDC 6600 computer.

The model had the capability of simulating start-up with the holdup and recycle tanks, and the crystallizers either full or empty. To fill a vessel, the inlet flows are summed at the integration time interval until the vessel is filled at which time overflow to the next vessel begins.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

Results

Various start-up schemes were tested to obtain a feel for the operation of the pilot plant and to identify difficulties. The rate of TNT production versus time from start-up is plotted in Figure 1 for the condition of continuous acid recycle. Curve "a" represents the condition that all vessels are initially filled with fresh acid at the composition of the dinitrator feed acid. In this case the concentration of DNT builds up dynamically in the dintrators. Curve "b" results when each dinitrator is premixed to its steady-state DNT concentration prior to the time of plant start-up. The proper DNT concentrations can be achieved by metering toluene batchwise into each acid-filled dinitrator. The latter procedure significantly shifts the start-up procedure towards shorter times and has the advantage of allowing an incremental start-up.

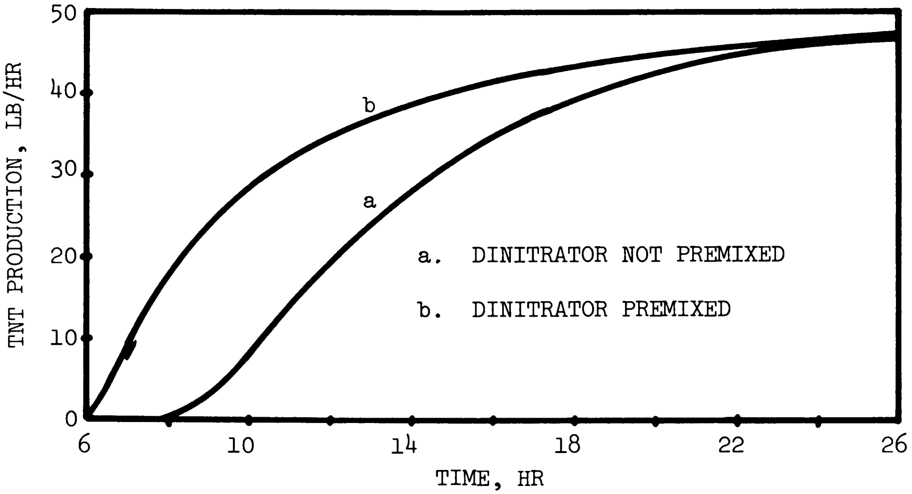


Figure 1. Start-up with closed-loop continuous recycle of acid

In Figure 2, initial operations using continuous and batch recycle of the dinitrator feed acid are compared. The initial plan was to collect and recycle the dinitrator acids in 200 gal batches, curve "c". The case of continuous, closed-loop acid recycle, curve "a", allows the system to reach steady-state quicker than for the batch recycle case. However, if the batch size is reduced to 100 gal, curve "b", then steady-state operation is achieved as quickly as for the case of continuous recycle. Approximately four hours would be required to collect a 100 gal batch of recycle acid. This period allows sufficient time for acid analysis and adjustment of acid concentration. Batch

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

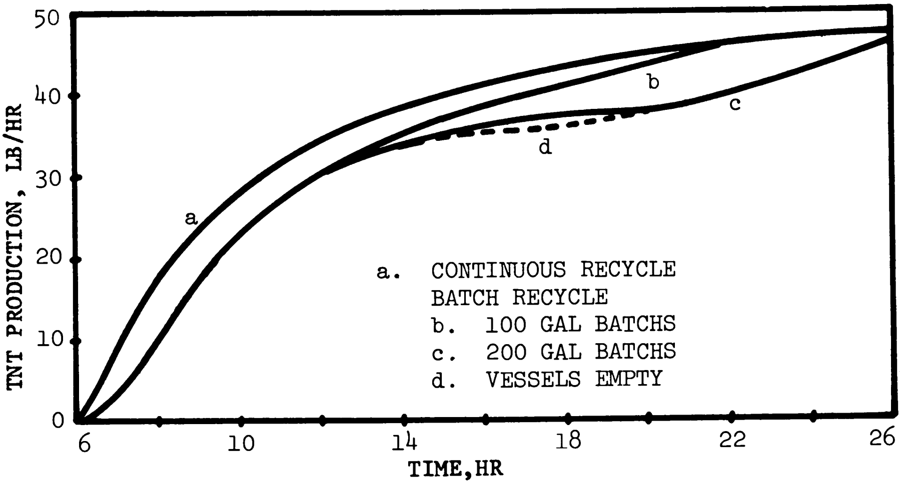


Figure 2. Start-up with dinitrators premixed using batch and continuous acid recycle

recycle is favored during start-up because of these operational considerations.

Curve "d" represents start-up when the hold-up tanks and crystallizers are empty and the recycle acid is collected in 200 gal batches. It was thought that start-up with the vessels empty would reduce the time to reach steady-state, since the empty vessels would fill with acid containing organics rather than with pure acids. However, for this system there is no time advantage by starting with the vessel empty.

One facet of start-up which was not expected is the disparity between the flow of recycle acid and the required flow of dinitrator feed, Figure 3. As the organics build up in the acids they displace their volume of acid and the extra acids appear in the recycle stream. The problem of generating excess recycle acid can be overcome by starting-up the process with the crystallizers partially empty. The change in recycle acid rate is another factor that would make start-up with continuous acid recycle very difficult.

The initiation of crystallization and the sequence in which the crystallizers become saturated was an area of concern during the design of the pilot plant. The dynamic build-up of TNT in the five crystallizers is shown in Figure 4. It can be seen that the steady state temperature profile is very undesirable during start-up: the crystallizers become saturated in the order #4, #5, #3, #2, #1. Under these conditions crystallizers #1, #2, #3, and #4 would have to be seeded independently to initiate crystallization. If the initial temperature profile is adjusted to produce saturation at concentrations along the diagonal line in Figure 4, then only the first crystallizer would

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

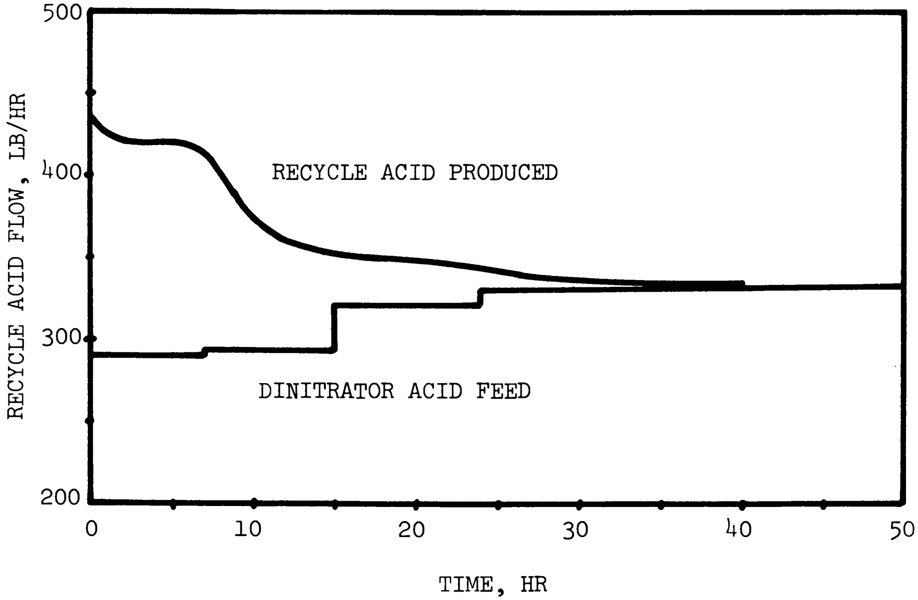


Figure 3. Production and utilization of recycle acid during start-up

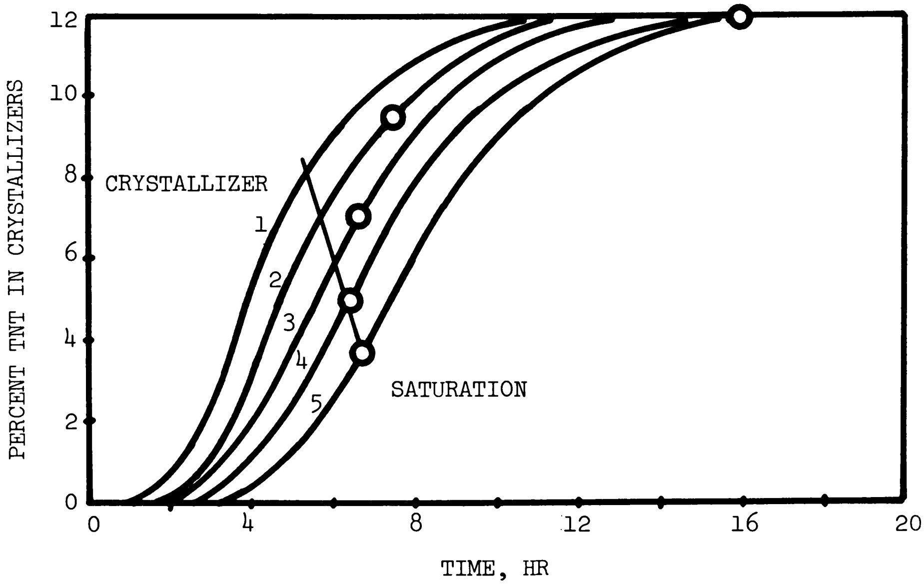


Figure 4. Build-up of TNT in the crystallizers, batch recycle, dinitrators premixed

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch019

have to be seeded. The crystallizer temperature would be adjusted to the steady-state values later in the run.

The ratio of HNO_3 to SO_3 and the amount of HNO_3 feeding the dinitrators are both critical control parameters. After dinitration the acid contains only 1% to 3% HNO_3. A slight error in the amount of HNO_3 going to the dinitrators could result in insufficient HNO_3 to nitrate all of the toluene. Free toluene is observed to complex with nitrosylsulfuric acid to form a black gummy complex, a situation which must be avoided. It was determined using the simulation that the concentration of HNO_3 in the last dinitrator falls to zero within one hour following a 10% reduction in HNO_3 feed. At the planned sampling rates, the upset could not be observed in time to avoid the zero HNO_3 concentration. Control of acid from the dinitrators must, therefore, be based on the analysis and flow rate of acid to the dinitrators.

The ratio of HNO_3 to SO_3 presents a different problem. An upset of 16% in the rate of oleum to the trinitrators would require 6 hours before producing a critical effect. Furthermore, the upset would be observed in the routine 4 hour acid analyses and could be corrected both at the source and by adjusting the acid concentration in the recycle acid hold-up tanks.

The model indicated that the trinitration reaction was essentally complete within the first trinitrator. The result is not unexpected since the trinitrator hold up is overdesigned in order to have vessels of sufficient size (25 gal) to provide scale-up data.

Conclusion

Computer simulation proved to be a useful tool in confirming the IITRI design and answering the questions regarding start-up and operation of the pilot plant. Collection and analyzing the recycle acid in 100 gal. batches appears optimal from the viewpoints of time to reach steady state and control of the process. Premixing of the dinitrators to their steady-state level will also shorten the start-up period and facilitate an orderly start-up. The pilot plant, as designed by IITRI, should be relatively simple to operate from a process standpoint. It is expected that the most difficult problems in running the plant will lie within the operation of individual components such as the filter unit.

Literature cited

1. Hoggett, J.G. et al, Nitration and Aromatic Reactivity, Cambridge University Press (1971) Great Britain, p.6.
2. Gillespie, R.J. and Graham, J., "Crvoscopic Measurements in Sulphuric Acid, Part V. Ionization of Nitric Acid in Sulfuric Oleum", J. Chem. Society, (1950), p. 2532 - 2537.
3. Goldstein, R., Computer Simulation of the Continuous TNT Process, Volume 1: The Nitration Section, Picatinny Arsenal Technical Report No. 4684 (1975) Dover, New Jersey, p. 23.

20

Isomer Control in the Mononitration of Toluene

G. F. P. HARRIS

Research Department, Imperial Chemical Industries Limited, Organics Division,
Hexagon House, Blackley, Manchester 9, England

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Introduction

It is well known that nitration of aromatic molecules produces a number of isomeric products. According to literature data (1) the mononitration of toluene can yield products in which the ratio of the orthonitrotoluene to paranitrotoluene varies between 1.41 and 1.62 depending on the nitrating agent and the reaction conditions used.

These mononitrations are carried out industrially on a considerable scale to produce compounds which are required as intermediates for the manufacture of dyestuffs, pharmaceuticals etc. In most cases the para isomer is required while the ortho and meta isomers are waste products. Thus with increasing costs of raw materials and environmental problems in disposing of waste isomers, any increase in the percentage of the desired isomer represents a considerable process improvement.

A wide range of nitrating agents have been used in laboratory scale experiments. Industrial scale nitrations, however, require a nitrating agent which is available in quantity, reasonably cheap and relatively stable. The work described below is an investigation of the isomer mixtures, one of which - sulphuric/nitric acid - has been in industrial use for many years, and a second mixture - sulphuric/nitric/phosphoric acid - which could be used for large scale nitration.

Experimental

All the nitrations were carried out on a laboratory scale in a 700 ml glass reactor fitted with a stirrer and cooling coil and mounted in a thermostated bath. The cooled nitrating mixture was added slowly to the toluene with vigorous stirring and the temperature of the reactor contents maintained at $45^{\circ} \pm 2^{\circ}C$. After the addition of the nitrating mixture was complete, the reactor contents were stirred for a further one hour to complete the reaction.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

The reaction products were then cooled, washed with water and the organic layer analysed by gas liquid chromatography for unchanged starting material, ortho, meta and para mononitro toluenes and for dinitration products.

In the early stages of the work a few experiments were carried out with different reaction temperatures and longer periods of stirring after the completion of addition. Increase in the length of the period of stirring had no effect on the composition of the reaction products. Decrease in reaction temperature did tend to increase the amount of para isomer produced, but it also decreased the rate of reaction, and any significant increase in the amount of the para isomer could only be obtained at the expense of a considerable decrease in the rate of reaction and consequently of the output of paranitrotoluene.

In view of these experiments 45°C was considered to be the optimum temperature for the nitration of toluene and all further experiments were carried out at this temperature.

Results

1. Sulphuric/nitric acid mixtures. This mixture has been used under varying conditions for industrial nitrations for many years, and there is a considerable amount of literature data on the reaction kinetics.

Information on the relationship between the composition of the nitrating mixture and the composition of the reaction product is, however, scarce and tends to be unsystematic.

There are three variables in the composition of the sulphuric/nitric acid nitrating mixture: (i) nitric acid content, (ii) water content, (iii) sulphuric acid concentration. A few preliminary experiments indicated that the concentration of nitric acid did not affect the composition of the reaction product as long as there was sufficient of it to mononitrate all the toluene present. Hence all further experiments were carried out with a slight excess of nitric acid - 1.04 mols HNO_3/mol of toluene. A series of experiments was then carried out to investigate the effect of the water and sulphuric acid concentrations in the nitrating mixture on the composition of the reaction products. The results of these experiments are illustrated by Figs. 1 - 5.

Fig. 1 shows a plot of reaction product composition vs. mols H_2SO_4 for a nitrating mixture which contains too little water for satisfactory mononitration. Excessive amounts of dinitration products are produced even at relatively low H_2SO_4 concentrations, and consequently considerable quantities of toluene remain unnitrated.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

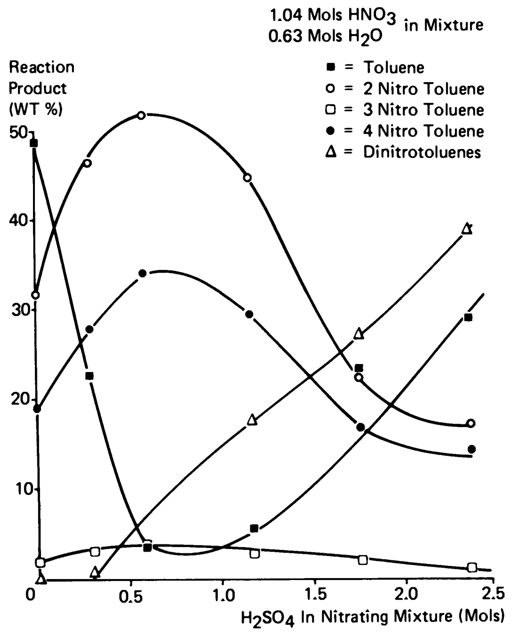


Figure 1. Reaction product composition vs. sulphuric acid content of nitrating mixture

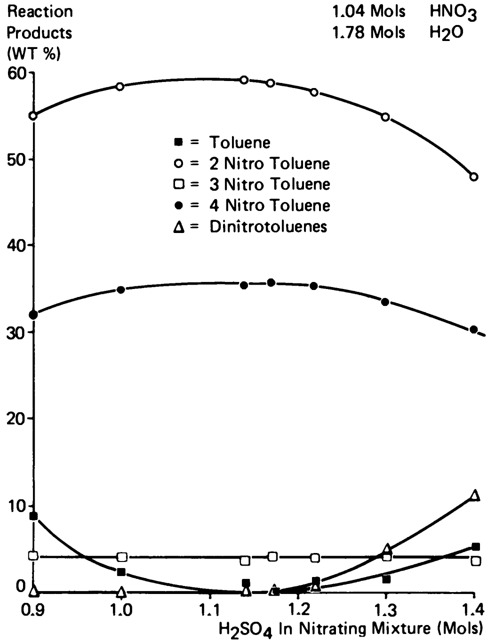


Figure 2. Reaction product composition vs. sulphuric acid content of nitrating mixture

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Fig. 2 shows a more satisfactory situation where there is more water (1.78 mols) in the nitrating mixture and reaction products containing only traces of unchanged toluene and dinitration products can be obtained. Fig. 3 shows the effect of variation in water content in a nitrating mixture containing 1.17 mols sulphuric acid - the optimum H_2SO_4 concentration in Fig. 2. In all these experiements the amounts of ortho and paranitro toluenes, unconverted toluene and dinitration products varied with water or sulphuric acid concentration, but apart from extreme conditions, (Fig. 1), the amount of metanitrotoluene remained constant at about 4%.

Figs. 4 and 5 show the effect of variation in sulphuric acid and water content of the nitrating mixture on the o/p isomer ratio of the mononitrotoluenes in the reaction products. O/p isomer ratio decreases with increase in sulphuric acid content of the mixture and increases with increase in water concentration. Examination of Fig. 1 shows that some of this decrease in o/p ratio with increase in sulphuric acid concentration is due to the fact that the o-nitrotoluene dinitrates more readily than the para isomer. Thus the increase in the amount of para isomer which can be produced by varying the composition of the nitrating mixture is limited if excessive amounts of dinitration products are to be avoided. In fact the optimum conditions for mononitration are shown in Fig. 2 - a nitrating mixture containing 1.17 mols sulphuric acid and 1.78 mols water giving a reaction product containing 36.5% p-nitrotoluene, 59.5% o-nitrotoluene and 4.0% of the meta isomer. o/p = 1.63.

2. Nitration in the presence of phosphoric acid.

Literature data (1) indicated that nitration in the presence of phosphoric acid increased the amount of p-nitrotoluene produced, hence a series of experiments was carried out using nitrating mixtures containing this acid. Concentrated phosphoric acid is a complex mixture of the ortho, pyro and meta acids (2), hence the phosphoric acid content of the nitrating mixture was expressed in terms of mols P_2O_5.

Initial experiments were carried out using a nitrating mixture of just phosphoric and nitric acids. Three strengths of phosphoric acid were used, 65.2% P_2O_5 (90% H_3PO_4), which is available commercially, and 72% P_2O_5 (99.2% H_3PO_4) and 78% P_2O_5 (107.5% H_3PO_4) which were prepared by adding extra phosphorus pentoxide to the commercial acid. In each experiment 1.04 mols 95% nitric acid (per mol of toluene) was added to a known amount of phosphoric acid and the nitration carried out as described above. The results of these experiments are shown in Figs. 6-8 inclusive, where the composition of the reaction products is plotted against mols P_2O_5 in the nitrating mixture for each of the three phosphoric acids used.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

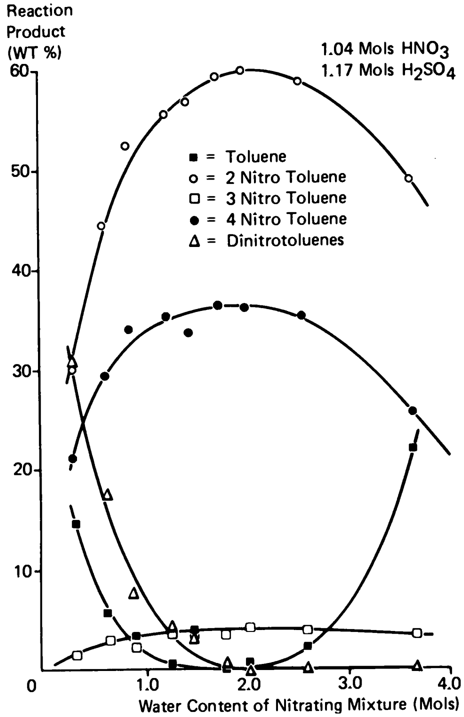


Figure 3. Reaction product composition vs. water content of nitrating mixture

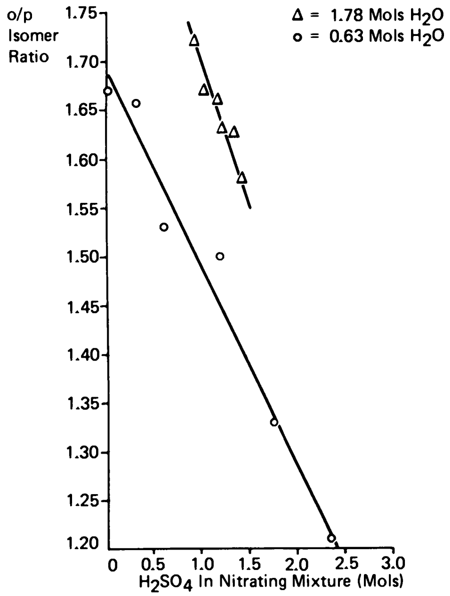


Figure 4. o/p isomer ratio vs. sulphuric acid content of nitrating mixture

Examination of these figures shows that none of the nitrating mixtures gives satisfactory nitration. The 65.2% P_2O_5 acid gives a very slow reaction with excessive amounts of unchanged toluene, while the 72% P_2O_5 acid produces considerable amounts of dinitration products if sufficient phosphoric acid is added to ensure complete nitration of the toluene. The 78% P_2O_5 phosphoric acid produces excessive amounts of dinitration even at low P_2O_5 concentrations. This was partly due to the viscous nature of this material, which gave rise to difficulties in mixing the reagents and to local overnitration. As in the experiments with sulphuric/ nitric acid mixtures the amount of metanitrotoluene was always about 4%.

Fig. 9 shows that for each of the three phosphoric acid systems used o/p isomer ratio decreases with increase in the amount of phosphoric present in the nitrating mixture, with the more marked decrease occurring for the two stronger phosphoric acids (72 and 78% P_2O_5). Examination of Figs. 6 - 8 shows that this decrease in o/p isomer ratio is due partly to an increase in the amount of paranitrotoluene produced and partly to the fact orthonitrotoluene dinitrates more readily than the para isomer.

As mentioned above, no mixture of phosphoric and nitric acids could be found to give the desired conditions of a product free from both unchanged toluene and dinitrotoluenes, but it can be seen from Fig. 6 that the presence of phosphoric acid in the nitrating mixture does reduce the o/p isomer ratio even when no dinitration products are formed.

The difference between the three phosphoric/nitric acid systems used is the amount of water present. Hence a second series of experiments was carried out to investigate both the effect of water and the addition of sulphuric acid to the nitrating mixture. The phosphoric acids used before were employed in these experiments and a slight excess of nitric acid - 1.04 mols/mol toluene was added in each case. The concentration of sulphuric acid was varied and the amount of water present in the nitrating mixture was controlled by varying the strength of the nitric acid used and adding the sulphuric acid as either 98% H_2SO_4 or fuming sulphuric acid. It was found that the phosphoric/nitric/sulphuric acid mixtures gave similar curves to those obtained previously, Figs. 2, 8, with product compositions varying with the amount of sulphuric acid, phosphoric acid and water present in the nitrating mixture. An increase in the amount of phosphoric acid (as mols P_2O_5) present gave a decrease in the o/p isomer ratio, while increase in the amount of water present had the opposite effect on isomer ratio. If too little water was present, however, excessive amounts of dinitration product were produced. Increase in the amount of sulphuric acid present also decreased o/p isomer ratio, but excessive amounts led to overnitration of the toluene.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

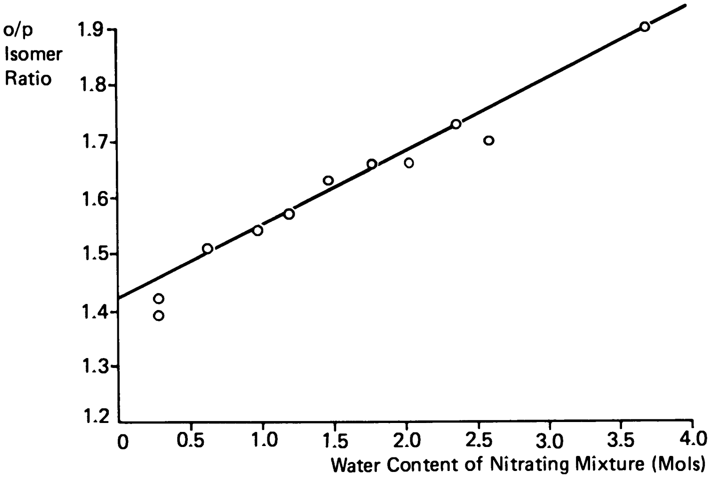


Figure 5. o/p isomer ratio vs. water content of nitrating mixture (H_2SO_4 content 1.17 Mols)

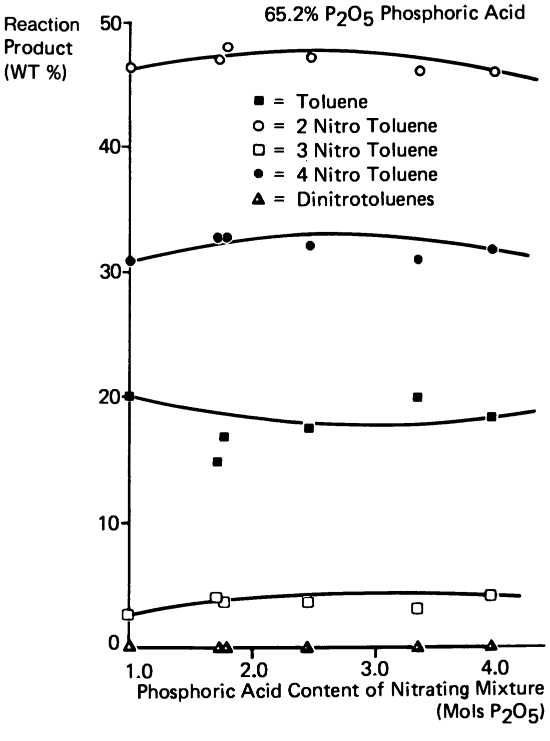


Figure 6. Reaction product composition vs. phosphoric acid content of nitrating mixture

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

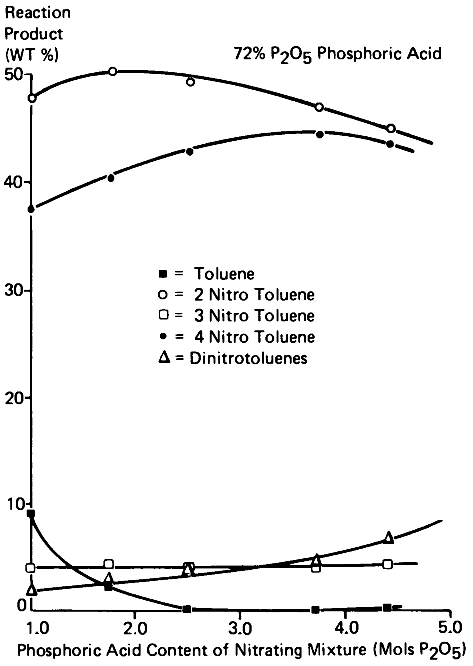


Figure 7. Reaction product composition vs. phosphoric acid content of nitrating mixture

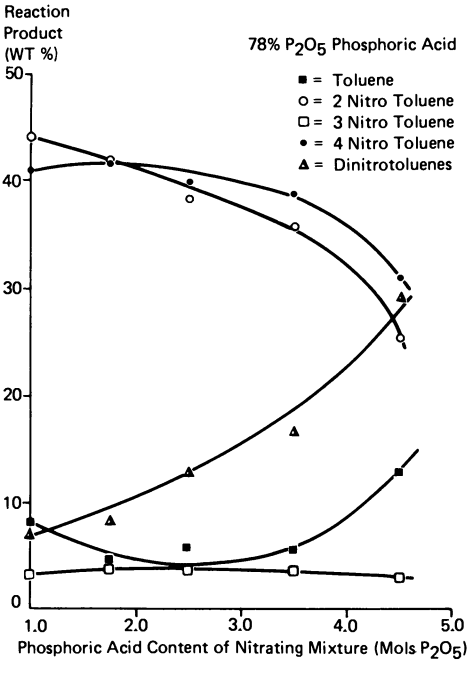


Figure 8. Reaction product composition vs. phosphoric acid content of nitrating mixture

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Certain nitrating mixtures gave products which were free from appreciable quantities of both unchanged toluene and dinitration products and also gave more p-nitrotoluene than obtained with the optimum sulphuric/nitric acid mixture. The compositions of these nitrating mixtures are shown in Table I, along with that for the best sulphuric/nitric acid mixture.

Table I

Optimum Nitrating Mixtures

Nitrating Mixture Comp.			Reaction Product Composition				o/p
Mols H_2SO_4	Mols H_2O	Mols P_2O_5	o-nitro toluene %	p-nitro toluene %	m-nitro toluene %	Toluene and Dinitro toluenes %	
0.2	9.1	2.5	53.5	40.9	4.8	0.8	1.31
0.95	9.9	2.5	55.0	40.8	4.2	0	1.35
1.17	10.0	2.3	55.7	40.3	4.0	0	1.38
1.17	1.78	0	59.5	36.5	4.0	0.2	1.63

Discussion

The above experimental results indicate that addition of phosphoric acid to the nitrating mixture does increase the amount of para isomer produced (Figure 9). Where appreciable amounts of dinitration occur, however, the position is complicated by the fact that the orthonitrotoluene dinitrates more readily than the para isomer and so the apparent effect of phosphoric acid addition is enhanced by conversion of some of the ortho isomer to dinitrotoluenes.

Two other variables affect the isomer ratio of the product - sulphuric acid concentration and water content of the nitrating mixture. Fig. 10 shows a comparison of the effect of the three variables - P_2O_5, H_2SO_4 and water content of the nitrating mixture on isomer ratio of the product for two systems containing phosphoric acid and one mixture of sulphuric and nitric acid. The region where no appreciable (less than 0.5%) dinitration products were produced is also shown. The adoption of a different convention to calculate the water content of the nitrating mixture (e.g. assuming that the phosphoric acid is all H_3PO_4 and not P_2O_5) could shift the phosphoric acid lines to the left, but it is clear that addition of phosphoric to the nitrating mixture does reduce the o/p isomer ratio of the product without producing unacceptable amounts of dinitration products.

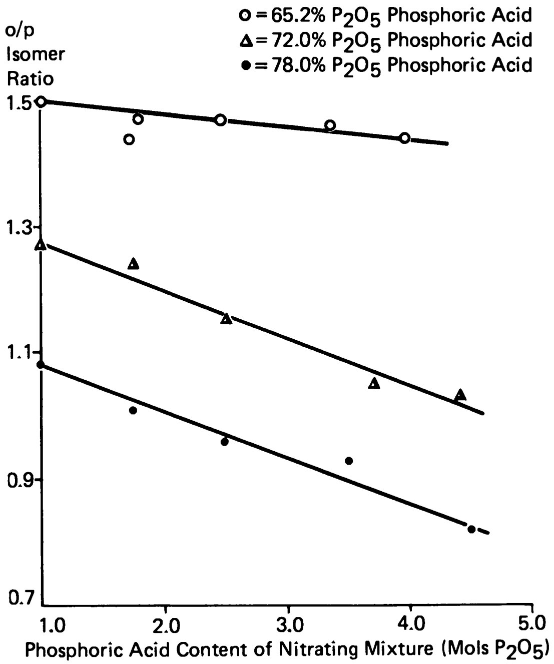


Figure 9. o/p isomer ratio vs. phosphoric acid content of nitrating mixture

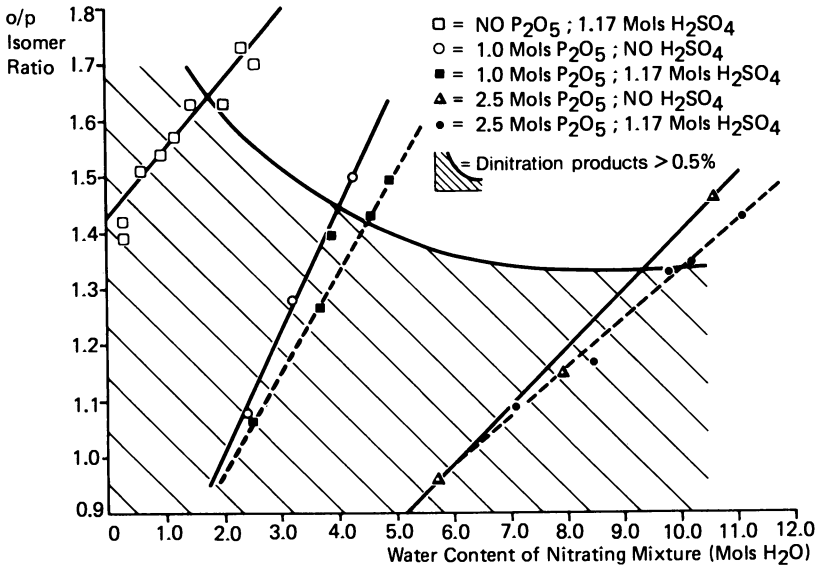


Figure 10. o/p isomer ratio vs. water content of nitrating mixture

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

This reduction in o/p isomer ratio is limited, however, to a minimum value of about 1.34.

The presence of sulphuric acid does tend to decrease the o/p isomer ratio slightly, but its effect is limited and excessive amounts produce quantities of undesirable dinitration products (Fig. 1). Its main advantage is to increase the amount of conversion so that large quantities of unnitrated toluene do not remain at the end of the reaction.

Considerable variation in the proportions of the isomeric reaction products from the mononitration of toluene have been reported by a number of workers, notably Tsang, Paul and Di Giamio (1) for nitration in the presence of phosphoric acid, Olah and Kuhn (3) for nitration by nitronium salts, and Wright, Teipel and Thoennes (4) for nitration in the presence of sulphonic acid ion exchange resins. All these workers attribute the variations in o/p isomer ratio in the nitration products to the effect of steric hindrance. The change in isomer ratio produced by the presence of phosphoric acid is probably due to this effect. Thus as postulated by Tsang et al. (1), it is likely that the attacking species in the nitration reaction is not the normal nitronium ion, but a bonded nitronium ion formed from the polymeric phosphoric acid and nitric acid. The steric bulk of this species together with the bulk of the methyl group of the toluene would favour substitution in the para position rather than ortho. Fialkov and Tarasenko (5) found that the electrical conductivity and viscosity data of phosphoric/nitric acid mixtures indicated the two acids did form a 1:1 complex, supporting the idea of a complexed nitronium ion.

Chlorobenzene is also mononitrated on a large scale in industry and, as in the case of toluene, the paranitrochlorobenzene is the isomer which is in demand while the ortho isomer has few uses. Unlike toluene, nitration with a H_2SO_4/HNO_3 mixture gives a mixture with a preponderance of the para isomer (63.8% para nitrochlorobenzene, 35.7% ortho o/p = 0.56 and only a trace of the meta isomer). However, any increase in the amount of the para isomer produced is important, and so a few experiments on nitration with mixtures containing phosphoric acid were carried out and the results are shown in Table II together with data for the nitration of chlorobenzene with the optimum sulphuric/nitric acid mixtures.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Table II

Nitration of Chlorobenzene

Nitrating Mixture Comp.			Reaction Product Composition					o/p
Mols H_2SO_4	Mols H_2O	Mols P_2O_5	Chloro benzene (%)	4 Nitro chloro benzene (%)	3 Nitro chloro benzene (%)	2 Nitro chloro benzene (%)	Dinitro chloro benzene (%)	
0	10.6	2.5	21.9	46.7	0	31.4	0	0.67
0	3.1	1.0	7.1	55.5	0	37.5	0	0.68
0	7.5	2.5	0.7	56.6	0	42.7	0	0.75
0	6.3	2.5	0	58.7	0	41.3	0	0.70
1.11	7.6	2.5	0	57.4	0	42.1	0.3	0.73
1.50	7.7	2.5	0	57.8	0	41.4	0.7	0.72
1.20	0.93	0	0.4	63.8	0	35.7	0.1	0.56

In view of the increased amount of para isomer produced by the nitration of toluene in the presence of phosphoric acid, the results in Table II seemed surprising. However, Sparks (6) found that nitration of chlorobenzene with nitric acid/acetic anhydride mixtures gave a lower o/p isomer ratio than when nitric/sulphuric acid was used, while toluene yielded essentially the same o/p ratio with each nitrating mixture. Sparks considers that this was due to the halogen substituent inducing a positive charge at the ortho position (relative to the para position). Interaction of this charge with the nitronium ion is enhanced in solvents of low dielectric constant (acetic acid as opposed to sulphuric acid), hence ortho substitution is correspondingly decreased in low dielectric constant solvents (acetic anhydride). It is possible that a similar mechanism applies in the above experiments with the phosphoric/nitric acid mixture having a higher dielectric constant than a mixture of sulphuric and nitric acids.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Literature Cited

(1) Tsang, Paul and Di Giamio, J. Org. Chem. (1964), 29, 3387.
(2) Bell, Ind. Eng. Chem., (1948), 40, (8), 1464.
(3) Olah and Kuhn, J.A.C.S. (1962), 84, 3684.
(4) Wright, Teipel and Thoennes, J. Org. Chem. (1965), 30, 1301.
(5) Fialkov and Tarasenko, Zh. Neorgan. Khim. (1966), 11(3), 619
(6) Sparks, J. Org. Chem. (1966), 31, 2299.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch020

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

21

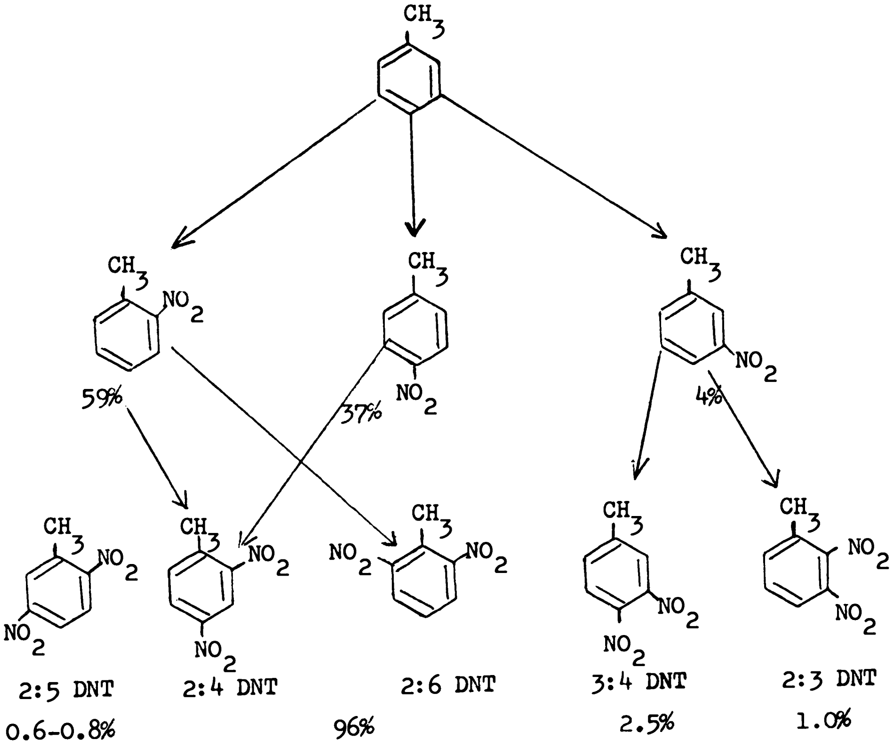
Control of Isomer Ratio in the Dinitration of Toluene

G. F. P. HARRIS

Research Department, Imperial Chemical Industries Limited, Organics Division,
Hexagon House, Blackley, Manchester 9, England

Introduction

Dinitrotoluenes are manufactured on a large scale to provide starting material for the production of isocyanates. As in the case of the mononitration of toluene a number of isomeric products are produced, viz.



Thus most of the toluene is converted to 2:4 and 2:6 dinitrotoluene.

When the standard sulphuric/nitric acid nitrating mixture is used these two isomers are produced in the ratio 80:20 2.4:2.6 dinitrotoluene, which is the desired ratio for isocyanate production. Some of the so called "ortho"-isomers 3:4 and 2:3 dinitrotoluene - are also produced and a small amount of 2:5 dinitrotoluene is present in the reaction products.

When the dinitrotoluenes are reduced to the corresponding amines and phosgenated for isocyanate production these "ortho" isomers do not react readily and give rise to quality problems in the final product. Hence there will be considerable benefits if the 2:3 and 3:4 dinitrotoluene can be eliminated from the nitration product or at least reduced in quantity.

In previous work on the mononitration of toluene (1) with nitrating mixtures containing phosphoric acid the amount of metanitrotoluene (the precursor of 2:3 and 3:4 dinitrotoluenes) could not be reduced, but it was possible to alter the isomer ratio of the reaction products so that the amount of ortho nitrotoluene produced was decreased.

As shown above, para nitrotoluene gives 100% 2:4 dinitrotoluene on further nitration, while the ortho isomer gives a mixture of 2:4 and 2:6 dinitrotoluenes. From the results of the work on mononitration of toluene it is possible that the presence of phosphoric acid during nitration of o-nitrotoluene would decrease the amount of 2:6 dinitrotoluene (ortho nitration) produced. Thus mixtures of o-nitrotoluene and toluene could be converted to dinitrotoluenes and still give the desired 80/20 mixture of 2:4 and 2:6 dinitrotoluene. This would also reduce the amount of 2:3 and 3:4 dinitrotoluenes, since nitration of o-nitrotoluene gives only the 2:4 and 2:6 isomers.

A series of experiments was carried out, therefore, on the dinitration of toluene/ortho nitrotoluene mixtures in the presence of phosphoric acid.

Experimental

The nitrations were carried out in a 700 ml glass reactor fitted with a stirrer and cooling coil and mounted in a thermostated bath. The cooled nitrating mixture was added slowly to the toluene/ortho nitrotoluene mixture with vigorous stirring and the temperature of the reactor contents maintained at 65 ±3°C. After the addition of the nitrating mixture was complete the reactor contents were stirred for a further 2 hours at 65°C to complete the reaction. The reaction products were then poured on to ice, filtered and the solid product dried and weighed. In a few experiments some liquid nitration products (mononitrotoluenes) were produced. These were recovered from the filtrate, washed, dried and weighed.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

1. Strength of phosphoric acid (% P_2O_5)
2. Concentration of P_2O_5 (mols)
3. Concentration of sulphuric acid (mols)
4. Ortho nitrotoluene/toluene ratio

As in the work on mononitration (1) the phosphoric acids were prepared by adding extra P_2O_5 to commercial phosphoric acid. The strengths of the acids produced were expressed in terms of (% P_2O_5) since concentrated phosphoric acid is a complex mixture of the ortho, pyro and meta acids.

The amount of nitric acid did not appear to be important as long as there was sufficient to convert all the toluene and ortho nitrotoluene to dinitrotoluene. A slight excess (1.04 mols HNO_3/mol orthonitrotoluene + 2.08 mols HNO_3/mol toluene) was, therefore, used in all subsequent experiments. It also appeared important to reduce the amount of water present to a low level so the nitric acid strength was fixed at 95% HNO_3.

The process was optimised in terms of the four variables listed above. A statistically designed series of experiments was carried out in which the four variables were each investigated at three levels, viz.

1. Phosphoric acid strength 68, 72 and 78% P_2O_5.
2. Phosphoric acid concentration 1.0, 2.5 and 4.0 mols P_2O_5.
3. Sulphuric acid concentration 2.0, 4.25 and 6.0 mols H_2SO_4 as 98% sulphuric acid.
4. Orthonitrotoluene/toluene ratio 0.2, 0.6 and 0.8.

27 Experiments - a ⅓ replicate of the full factorial of experiments with 4 variables - were carried out and the results analysed statistically. The orthonitrotoluene/toluene ratio was used as the response and each of the independent variables as linear and squared terms. All the square terms were rejected and the equation fitted was

$$\text{ONT/Toluene Ratio} = 0.69 + 0.08\,(x - 4)^{\frac{1}{2}} + 0.11\,(y - 73)^{\frac{1}{5}} + 0.13\,(z - 4)^{\frac{2}{3}} - 0.70\,(R - 4)^{\frac{2}{3}}$$

where $x = H_2SO_4$ conc. (mols)

$y =$ phosphoric acid strength (% P_2O_5)

$z = P_2O_5$ conc. (mols)

$R =$ 2:4/2:6 dinitrotoluene isomer ratio

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

Solid and liquid reaction products were analysed separately by gas liquid chromatography for unchanged starting material, mononitrotoluenes and the five dinitrotoluenes, and the percentage conversion to each reaction product and the 2:4/2:6 dinitrotoluene ratio calculated.

A few samples were analysed by infra red methods to check the accuracy of the GLC method of analysis. The 2:4/2:6 isomer ratios determined by the two methods agreed well for samples which contained less than about 3% "ortho" isomers (2:3 and 3:4 dinitrotoluenes). If more than this amount of "ortho" isomers was present infra red measurements gave too high a value of the isomer ratio.

Results

1. Blank Experiments on Toluene Nitration. Under manufacturing conditions the nitration of toluene with a mixture containing 64.0 wt.% H_2SO_4, 27.2% HNO_3 and 8.8% water gives a reaction product with 2:4/2:6 dinitrotoluene isomer ratios of 4.0 - the desired mixture for isocyanate production. Laboratory scale experiments on the nitration of toluene with this mixture gave a product with an isomer ratio of 4.37 and "ortho" isomer content of 3.6%.

This increase in the amount of 2:6 dinitrotoluene in the reaction product is probably a scale effect due to differences in agitation and method of adding the nitrating mixture between the laboratory and manufacturing scale equipment.

2. Nitration of Orthonitrotoluene. Initial experiments were carried out on the nitration of orthonitrotoluene alone. The standard sulphuric/nitric acid mixture was used with the addition of phosphoric acid. It was found that a 2:4/2:6 isomer ratio of about 3.0 could be obtained by using large quantities of polyphosphoric acid. Though this was an improvement on the ratio of 1.86 obtained when no phosphoric acid was present in the nitrating mixture, it was less than the 4.0 isomer ratio necessary for isocyanate manufacture. All further work was, therefore, carried out with toluene/orthonitrotoluene mixtures.

3. Toluene/Orthonitrotoluene Mixtures. Preliminary experiments showed that the presence of some sulphuric acid (as well as phosphoric acid) in the nitrating mixture was desirable to give rapid conversion to dinitrotoluene. These experiments indicated that the following four variables affected the isomer ratio produced in the nitration of toluene/ortho nitrotoluene mixtures.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

The percentage fit of this equation was 87% and the residual standard deviation was 0.10 with an F value significant at the 0.1% level. Thus the major causes of variation have been considered and the linear relationship is of the correct order. This equation enables the relationship between orthonitrotoluene/toluene ratio in the nitration feedstock and the 2:4/2:6 dinitrotoluene isomer ratio of the product to be calculated for any given nitrating mixture with a composition within the experimental range.

The amount of "ortho" isomers in the reaction product varied considerably with reaction conditions. Table 1 shows the results of a series of experiments with a range of phosphoric acid strengths, mol. concentrations of P_2O_5 and H_2SO_4 and orthonitrotoluene/toluene ratios.

Table I

Orthonitro-toluene/toluene ratio	Phosphoric acid strength (% P_2O_5)	Phosphoric acid conc. (mols P_2O_5)	Sulphuric acid conc. (mols H_2SO_4)	% "Ortho" isomers in reaction product	2:4/2:6 dinitro toluene ratio
0.2	68	1.0	6.0	1.9	4.48
0.2	72	4.0	6.0	2.0	5.20
0.6	68	4.0	6.0	1.5	4.01
0.6	78	4.0	2.0	1.7	4.16
0.8	78	4.0	6.0	1.4	4.30
0.8	68	1.0	4.25	1.4	3.37
0.8	72	1.0	6.0	1.3	3.51

As anticipated the amounts of "ortho" isomers decrease with increase in the amount of orthonitrotoluene in the mixture being nitrated. The minimum quantity of ortho isomers in the reaction product was 1.3% compared with 3.5% for the nitration of toluene alone with a sulphuric/nitric acid mixture.

Discussion

Examination of equation (1) shows that there is no optimum, within the range of the experiments, in the amount of phosphoric acid used. The stronger the acid and the greater the number of mols P_2O_5, the larger the orthonitrotoluene/toluene ratio which can be used in the reaction mixture to give a particular 2:4/2:6 isomer ratio.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

There are, however, practical limitations to the reaction conditions which can be employed. Phosphoric acid containing more than about 78% P_2O_5 is too viscous to handle, while more than about 4.0 mols P_2O_5 in the nitrating acid gives very large volumes of reacting mixture.

Since the laboratory scale blank experiments with toluene alone and a sulphuric/nitric acid nitrating mixture gave a value of 4.37 for the 2:4/2:6 isomer ratio this figure was substituted in equation (1) and the orthonitrotoluene/toluene ratio calculated for a range of phosphoric acid strengths, number of molecules P_2O_5 and sulphuric acid. The results of these calculations are shown in Table II.

Table II

Calculated Values of ONT/Toluene Ratio to give an Isomer Ratio of 4.37

A

H_2SO_4 Conc. (mols)	6.0	6.0	4.25	4.25	4.25	4.25
Phosphoric Acid Strength (% P_2O_5)	78	78	78	78	72	72
P_2O_5 conc. (mols)	4.0	2.5	4.0	2.5	4.0	2.5
ONT/Toluene to give Isomer Ratio of 4.37	0.59	0.42	0.52	0.35	0.26	0.09
Wt. % Orthonitrotoluene in feedstock	46.5	38.5	43.6	34.2	27.9	11.8

Thus with a nitrating mixture containing 4.0 mols P_2O_5 as 78% P_2O_5 phosphoric acid together with 6.0 mols H_2SO_4 as 98% sulphuric acid (column A - Table 2) it is possible to use a feedstock containing up to 46.5% by weight orthonitrotoluene and still produce a product with the desired 2:4/2:6 dinitrotoluene isomer ratio. Such a product would contain about 1.7% "ortho" isomers.

Nitration in the presence of phosphoric acid, therefore, serves the purpose of providing an outlet for a waste product (orthonitrotoluene) from the mononitration of toluene, and reduces the amount of undesirable "ortho" isomers in the reaction product. It has a further advantage in reducing the amount of nitric acid required to produce dinitrotoluene, since it is only necessary to introduce one nitro group into the ortho nitrotoluene in the toluene/orthonitrotoluene mixture.

Literature Cited

1. Harris, G.F.P. Isomer Control in the Mononitration of Toluene - American Chem. Soc. Symposium, Philadelphia, April 1975 (This volume).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch021

22

Safe Manufacture and Handling of Liquid Nitric Esters

G. S. BIASUTTI

Dr. Ing. Mario Biazzi Soc. An., Quai Maria Belgia 18, Ch-1800 Vevey, Switzerland

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

The industrial manufacture of nitric esters began with the discovery by Alfred Nobel that the enormous power released by the explosive decomposition of nitroglycerine could be harnessed and used. Inadequate knowledge of this blasting oil's properties has been the primary cause in the past of many explosion disasters in all parts of the world. Slow but constant progress towards better safety was made during the following 40 years. Nevertheless, due to fast growing demand, the amount of nitroglycerine being manufactured increased manifold and, with it, the number of accidents and their destructiveness.

The first important step towards safer manufacture was made when Arnold Schmid, in 1927, designed and produced his first continuously operating nitration plant.

Then, in 1935, Mario Biazzi, a young Italian engineer, came out with a new process where great emphasis was placed on safe manufacture. Biazzi's ideas were based on the assumption, which was later proved not quite true, that nitroglycerine could not shoot when finely emulsified with another immiscible liquid. Based on this belief, Biazzi built his nitrator so as to create within, by means of a turbine wheel, a powerful and turbulent liquid flow. The nitroglycerine formed an extremely fine emulsion with the nitrating acid.

Even with lack of proof that this emulsion would not propagate a detonation, Biazzi obtained some interesting results from his nitrator design. The much improved mixing effect resulted in a greater reaction speed and better heat transfer, thus allowing a reduction in the size of the apparatus.

Washing of the nitroglycerine was performed under the same powerful agitation. Under these conditions it was possible to neutralise the acidic oil directly with a soda solution, thus eliminating the need of a pre-wash. Separation of the oil phase from the acid or wash water was carried out by exploiting the coalescing effect produced when a slow rotating movement is given to the two liquids.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

The result of these improvements was a great reduction of the quantity of explosive being present at any time in the equipment.

Over the years, the Biazzi process has been further improved and remote control introduced but its essential features have been little changed from the original design.

Other continuous processes for the manufacture of nitroglycerine were developed in the late fifties; the Swedish injection process and the Hercules tube nitrator. Both these processes are based on the nitration of glycerine in a turbulent flow of pre-cooled and diluted acid, coupled with centrifugal separation.

It is not the scope of this paper to describe the Biazzi process in its details or to compare it with other processes. Rather, I wish to emphasise those features of design and operation that have contributed to an increase of safety in the manufacture, transport and further processing of liquid nitric ester.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

Production Control

Safety can be improved by installing automatic or remote alarm and control systems that prevent, with or without the intervention of personnel, the occurrence of abnormal conditions. These control systems must be fail safe, i.e. in case of failure they must keep the plant in a safe condition. Further, they must not hide other failures which, otherwise, would be apparent. For instance, a thermostatic control of a reaction would not make it possible to detect a failure in the cooling system until the last moment, which could be too late.

Briefly, the basic automatic controls which are applied to the Biazzi installations for the manufacture of nitric esters and many dangerous nitrobodies are the following:

Ratio control of the reactants
Temperature control
Interface level control

These controls have been developed along conventional lines and need no further explanation. It is more interesting to consider what measures have been taken to prevent failures of the automatic control system. It must also be stressed that calculation of the nitration ratio (ratio of polyol to nitric acid) is often left to the empirical judgement of the operator.

It is known that the spent acid resulting from the nitration of poly-alcohols contains a variable amount of dissolved nitric ester which, even at ambient temperature, can go through an exothermic process of hydrolysis. This reaction, accelerated by a temperature increase, can easily go out of control. If this happens when the acid is still in the stage of separation from the nitric ester, it will almost certainly end up in an explosion.

This problem was investigated by Biazzi and his co-workers and the conditions were found under which the spent acid produced from the nitration can be considered safe.

The method of determining the stability of the spent acid was based on the nitrous acid formed from the oxidation reaction as a function of time at constant temperature. The determination was made on synthetic spent acids saturated with the nitric ester. The amount of NO_2 formed was measured by electrometric analysis, keeping the sample for three hours at 70°C.

As only NO_2 in the acid acts as a catalyst for further oxidation of the nitric ester, it is easy to determine from the shape of the asymptotic curve the limits of its stability. It was found that the stability of the spent acid is a function of its nitric acid content and of the molar ratio H_2O/H_2SO_4. Diagrams have been drawn up after extrapolation to a temperature of 35°C to show what is likely to occur in an operating plant.

The next question is how to determine, in the continuously operating plant, the stability of the spent acid.

Öhman in 1938 and Biazzi in 1952 investigated the possibility of determining the stability of the nitroglycerine spent acid by measuring the Redox potential. This method proved to be an extremely precise one for control of the nitration process. Since 1955 all Biazzi nitrators have been equipped with a Redox control system, through which any deviation from the normal nitration ratio during operation of the plant is immediately signalled and corrective steps can be taken manually or automatically.

At start-up, the Redox value is lower than at steady state due to the higher water and nitrous acid contents of the acid used for displacement on the previous run. After some time the Redox potential becomes perfectly constant. Knowing the exact composition of a reference solution, the absolute amount of nitric acid in the spent acid can be determined. A high Redox value, corresponding to a low nitric acid content in the spent acid, will give an alarm or possibly shut down the plant.

Neutralisation of the nitric ester flowing out from the separator is usually done in Biazzi plants by direct treatment with a concentrated sodium carbonate solution. Automatic control of this reaction has been achieved by means of a pH-meter which controls the soda water flow as a function of the pH of the emulsion leaving the washer.

In the event of malfunctioning of this instrument, a second pH-meter, the electrode of which is placed after the second or third washer, shuts down the plant.

In order to illustrate the sequence of events in an unusual situation, let us describe what happens in the case of a total electric power failure.

This failure will be detected by any one of the following failures:

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

1. slowing down of nitrator or washer stirrers
2. low brine pressure
3. low mixed acid flow

and the corresponding alarms will appear on the panel.

The sliding arm feeding the glycerine to the nitrator will immediately retract, preventing any glycerine from entering the reactor.

The control and alarm systems remain energized by DC power and compressed air.

The nitrator stirrer gradually slows down. Nevertheless, due to the heavy flywheel, the time is sufficient to complete the reaction. The same happens to the washers but, in these vessels, agitation is immediately restored by compressed air bubbling through the bottom.

One minute later, unless the operator intervenes, the automatic displacement process begins: spent acid flows from an overhead tank through the nitrator and slowly displaces the organic phase to the separator. The nitric ester flows further to the washers as in normal operation until it reaches the top overflow. When the washing time has elapsed, the bottom valves of the washers are opened and the emulsion flows to storage.

In conclusion, it can be said that the Biazzi production plant for nitric esters operates in the absence of personnel under very acceptable safety conditions.

Transport and Storage

The situation may not be the same for the further steps of transport, storage and processing.

From a survey we have made covering accidents related to liquid explosives, there is no doubt that the greatest frequencey and destructiveness is to be found in those originated during the storage, transfer and handling operations. We have recorded at least four cases of lightning striking the storage house and causing total destruction of the plant. However, most of the accidents were undoubtedly due to human failure.

The need to store nitroglycerine is due to the transition from a continuous to a batch process. If the further operations of weighing and mixing the nitroglycerine with other ingredients were to be continuous, no storage whatever would be required.

This has been partially achieved in Japan and Sweden for the manufacture of commercial explosives. In a 1,200lbs/hr plant, only 40kg of nitroglycerine and 20kg of dynamite are present at any time.

Safety in the storage of liquid explosives has been improved by Biazzi through the application of automation and remote control. The concentration of a large quantity of explosive in one place must still be avoided.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

Transfer of liquid explosives inside the factory has been in the past the source of a great number of accidents.

The old-fashioned method of carrying the nitroglycerine from one building to another in hand-driven wheel carts has not been abandoned and has even regained popularity after several disasters caused by the transmission of a detonation through the transfer pipe or gutter connecting two buildings.

The method of transferring an explosive liquid through a pipe line as a water emulsion was introduced by Biazzi in 1950 and later adopted in many factories before the mechanism by which an explosion can be initiated in a liquid had been investigated by, amongst others, Bowden and Yoffe. They demonstrated (1952) that a sudden change of pressure in the liquid could cause, by adiabatic compression of air bubbles, a temperature increase sufficient to trigger a detonation of the surrounding explosive.

In order to prevent an initiation due to adiabatic compression, the energy changes (pressure, temperature, velocity) within the system must be as gradual as possible. These changes occur when the system goes from a state of rest to the steady state of transfer, and vice-versa. A gradual change can be obtained by slowing down this transition period, in other words by slowing opening the water valve to the transfer ejector.

Another important energy change occurs within the ejector itself where, due to the decreasing cross-section of the pipe, the liquid explosive is subjected to a considerable acceleration. After having measured the energy changes inside an experimental ejector provided with a great number of piezoelectric elements, Biazzi designed and constructed a new type of ejector where these changes are kept near the theoretical minimum. This new ejector has been installed in several plants and no accidents have been reported with its use.

Once initiated, a detonation will propagate, under certain circumstances, through a water emulsion, causing the explosion of the entire mass of the nitric ester. In recent years much work has been done in order to find out the conditions under which the transmission of an explosion through a water emulsion cannot take place.

It was found that these conditions are primarily dictated by the critical diameter of the mass, which is a constant for each type of explosive.

For nitroglycerine, the critical diameter is a few millimeters. However, if the explosive oil is emulsified with water, the diameter is of the order of 20 millimeters, depending on the volume ratio between the two liquids. According to the above theory,which has been confirmed by experimental data, a detonation will not propagate through a pipe of a diameter of 20 millimeters where an emulsion of three parts in volume of water and one part of nitroglycerine travels at such speed that turbulent flow is maintained.

Based on this knowledge, Biazzi has designed and produced an entirely remote controlled and automated system which handles the liquid explosive from the outlet of the nitration unit to the delivery into the mixing plant, without the presence of personnel.

Future Developments

In conclusion, it can be said that the manufacture and handling of nitroglycerine and other nitric esters has reached an unprecedented stage of safety. Nevertheless, the chances of an accident still exist. Is there any way of further improving the safety conditions?

Evidently, once the personnel have been removed from the area exposed to a potential explosion, the accident will cause only material damage. If this line of thought is accepted, the next step is to reduce the chances and the destructiveness of an accident.

Detecting at the earliest possible stage the onset of decomposition in the manufacturing equipment is, for instance, one of the areas which could be further improved. The first sign of decomposition in a nitric ester is the formation of nitrous acid. In the presence of air, it forms the characteristic reddish-brown fumes. A continuous monitoring system, based either on photoelectric and colorimetric detection or on chemical analysis, could be conceived, which would give an alarm and operate the safety devices upon detection of nitrogen oxides in the air above the liquid being processed. Another approach would be determination of NO_2^- ions in the presence of NO_3^- ions by electrometrical analysis. Selective electrodes of this type have been developed.

Another problem open for research is a continuous determination of chemical stability of the finished nitric ester. It is known that nitric esters are very sensitive to traces of nitrous oxides, which have a catalytic effect on thermal decomposition reactions. Their chemical stability is usually tested by means of the Abel heat test, based on qualitative detection of minute amounts of nitrogen oxides in the air above a sample heated at 180°F. This time-wasting and unreliable method cannot easily be adapted to continuous monitoring. Ideas for better methods have been put forward but, to my knowledge, none has received practical application.

A further need, which has been pointed out in this Symposium, is completion and extension to nitric esters of knowledge on reaction kinetics, mass transfer and the formation of side products.

It is our opinion that the ways to be followed in future to improve safety, which generally coincide with economics, are:

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

1. further development of automation by applying more refined methods for determination of the reaction conditions and of the chemical stability;
2. reduction in the accumulation of dangerous products by using the continuous process, not only for their manufacture but also for their further handling.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch022

23

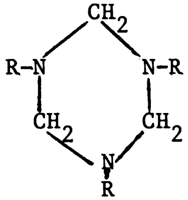
The Preparation of RDX from 1,3,5-Triacylhexahydro-s-triazines

E. E. GILBERT, J. R. LECCACORVI, and M. WARMAN

Explosives Division, Picatinny Arsenal, Dover, N.J. 07801

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

RDX (1,3,5-trinitrohexahydro-s-triazine, 1) has been an important military explosive since World War II. It is made by the nitrolysis of hexamethylenetetramine in the presence of ammonium nitrate and acetic anhydride, about 2 lbs. of anhydride being required per lb. of RDX. (The equations for this process are given later.)



1, R = NO_2

2, R = $SO_3^{\ominus}$

4, R = CH_3CO-

5, R = C_2H_5CO-

17, R = C_2H_5OCO-

20, R = $4-CH_3C_6H_4SO_2-$

Another procedure for the preparation of RDX, developed in Germany by Wolfram in the 1930's, involves nitrolysis of the hexahydro-s-triazine derivative 2 (as the potassium salt) (1). Although good yields of RDX were obtained, this method was abandoned as economically inferior to the other approach cited above. Brief attempts in the past to prepare RDX by the nitrolysis of two other hexahydro-s-triazine derivatives, 17 and 20, gave none of the desired product (2, 3).

Speculation during World War II as to the possible reaction sequence occurring during the preparation of RDX from hexamethylenetetramine and acetic anhydride, by the method cited above, led to the thought that compound 4 might be the key intermediate (3). This idea could not be tested at the time, since 4 was actually unknown until several years later, when a simple method for preparing it and some analogues was developed. Then, D.N. Thatcher did indeed show (4) that RDX could be prepared by the nitrolysis of 4 or 5. (It should be mentioned that, even though 4 can be nitrolyzed to RDX, and even though we have shown that 4 can be made by reacting hexamethylenetetramine with acetic anhydride (5), 4 is no longer considered to be an intermediate in the preparation of RDX by the direct nitrolysis of hexamethylenetetramine in the presence of acetic anhydride.)

Since a process of this type - involving the use of 4, 5, or similar compounds, as intermediates - appeared to us to be of potential interest for preparing RDX on a large scale, it seemed desirable to study the nitrolysis of other hexahydro-s-triazines to establish the optimum structure of R. We report herein the results of such a study, involving the nitrolysis of a series of known hexadydro-s-triazine derivatives, as well as of a number previously unknown; all of these are listed in Table I. In addition, we have studied variations in the nitrolysis procedure for compounds of special interest, toward developing an optimum preparative approach for 1. The conclusions reached after an economic analysis of this method, in comparison with the established method, are also summarized.

Screening of Candidate Triazine Compounds

In considering nitrolysis reagents suitable for this study, reference was made to the fairly extensive published data on the synthesis of secondary nitramines by the S_E2 nitrolysis of N,N-disubstituted amides and sulfonamides (6,7,8):

$$R_2NCOR' \longrightarrow R_2NNO_2 + R'COOH$$
$$R_2NSO_2R' \longrightarrow R_2NNO_2 + R'SO_2OH$$

Reagents used in these studies include: absolute nitric acid, nitric acid-phosphorus pentoxide, nitric acid-trifluoroacetic anhydride, nitric acid-acetic anhydride, and nitrogen pentoxide. For our purposes, the last two reagents were eliminated, since the former gave poor yields, and the latter is somewhat inconvient for routine laboratory use. The nitric acid-phosphorus pentoxide approach was retained, since it was reported to give an 84% yield of 1 from 2 (1), even though poor results were noted by others (7) in the nitrolysis of di(n-butyl) formamide with this reagent.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

The nitric-trifluoroacetic anhydride system was of special interest, since it was reported to give outstanding results in the nitrolysis of open-chain amides (6,7,8). Past work with this system has always entailed the use of 1.1 moles or less of nitric acid per mole of anhydride. When applying this stoichiometry in the nitrolysis of 4, only two of the three acetyl groups were nitrolysed, leading to the precipitation of 1-acetyl-3,5-dinitrohexahydro-s-triazine ("TAX"). (This comprises a new and improved procedure for preparing TAX, as described in the Experimental Section.) It was then found that use of 4.8 moles of nitric acid per mole of anhydride gave nearly complete nitrolysis of 1, since the excess nitric acid apparently functions as a reaction solvent, in contrast to trifluoroacetic acid (9). This stoichiometry was therefore used throughout in our studies.

The nitrolyses, all effected with large excesses of the reagents, gave the results summarized in Table I. Nitric acid alone consistently gave the lowest yields, and nitric acid-trifluoroacetic anhydride gave the best, except in the case of 4. The nitrolysis appears quite sensitive to structural factors, and (except for 18) is specific for R=alkanoyl as being the only substituting group yielding 1. Lengthening the chain (as in 5, 6, and 7) gives decreasing yields with all three reagents. Also noteworthy is the fact that 3 gave no 1, since several N,N-dialkylformamides have been shown (7) to give good yields of nitramines, especially with nitric acid-trifluoroacetic anhydride. However, no nitramines could be obtained from N,N-dialkylformamides with bulky alkyl groups (6). Branching the chain in the position of R by increasing the number of methyl groups (as in 5, 8, and 9) leads to a sharp decrease in yield, with little or no 1 being formed from the most highly substituted compound 9. A similar steric effect was noted previously in a study of the nitrolysis of N,N-dialkylamides (6). It is noteworthy that the nitric-trifluoroacetic anhydride system is less sensitive to steric factors than the other two, and, in fact, gave a low yield of 1 from 9 in contrast to the other systems, which gave none.

The presence of electron-withdrawing groups (i.e. Cl in 10, and CH_2=CH in 13) prevented the formation of 1. Robson and Reinhart (6) noted a similar effect in the nitrolysis of N,N-dialkylamides, and concluded that such groups reduce electron density at the amino nitrogen, thereby reducing the ease of electrophilic replacement of the acylium group. This suggested that electron-donating groups (as CH_3O in 11 and 12) might enhance the yield of 1, but no product was obtained. Robson and Reinhart made a similar observation.

Dimethylnitramine has been prepared by the nitrolysis of N,N-dimethylbenzamide (1), but we were unable to obtain 1 from 14. Interposition of a CH_2 group between the phenyl and CO groups, (15), likewise failed to yield 1. Steric considerations alone appear insufficient to account for this, in view of the fair to excellent yields of 1 obtained from 8.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

Table I

Nitrolysis of 1,3,5-Triacylhexahydro-s-triazines and Related Compounds

Compound	R	Ref. to Prepn. of Substrate	Yield[a] of 1 via HNO_3-P_2O_5	HNO_3 Alone	HNO_3-$(F_3CCO)_2O$
3	HCO	b	0	0	0
4	CH_3CO	5	95	15[c]	80[d]
5	C_2H_5CO	5	80	55	98
6	n-C_3H_7CO	5	60	40	94
7	n-$C_5H_{11}CO$	b	40	30	69
8	$(CH_3)_2CHCO$	b	50	30	94
9	$(CH_3)_3CCO$	b	0	0	15
10	$ClCH_2CO$	10	0[e]	-	0
11	CH_3OCH_2CO	b,e	0[e]	-	-
12	$CH_3O(CH_2)_2CO$	11	0[e]	-	-
13	CH_2=CHCO	12,13	0[e]	-	-
14	C_6H_5CO	12,13	0	0	-
15	$C_6H_5CH_2CO$	b	0	0	0
16	CH_3OCO	14	0	-	0
17	C_2H_5OCO	14	0	-	0
18	$K^{\oplus}\ {}^{\ominus}OCO$	b	-	30	30
19	CH_3COO	f	0	-	0
20	4-$CH_3C_6H_4SO_2$	15	0	-	-
21	CH_3SO_2	15	0	-	-

(Notes for Table I on next page)

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

Notes for Table I

a Mole percent yield of pure 1, based on the starting compound, except as noted.
b New compound, cf. Experimental Section.
c The crude product also contained 25% TAX.
d The crude product also contained 4% TAX.
e Private communication, Dr. M.D.Coburn, Los Alamos Scientific Laboratory.
f Cf. Experimental Section for improved preparation.

In confirmation of earlier work (2) in which nitric acid alone was used, no 1 could be obtained by nitrolysis of the carbamate 17; similar results were noted with 16. Past attempts to prepare nitramines from other cyclic, as well as open-chain, carbamate esters have also proved fruitless (1, 6). It was shown that cleavage of the alkyl-N bond occurred in preference to the desired acyl-N cleavage. In this study, a similar reaction would result in rupture of the ring. It is interesting that N-fluorocarbamate esters can be converted to nitramines in good yield (16).

Hydrolysis of either 16 or 17 with alcoholic potassium hydroxide gave a salt-like compound which could not be obtained pure and identified, but which did yield 1 upon nitrolysis, and to which structure 18 is tentatively assigned. Franchimont (17) noted that the calcium salt of N,N-dimethylcarbamic acid did not yield dimethylnitramine upon nitrolysis, but is merely converted to dimethylammonium nitrate:

$$[(CH_3)_2NCOO^-]_2\ Ca^{++} \not\longrightarrow (CH_3)_2NNO_2$$

if similar reasoning is applied to the nitrolysis of 18, intermediacy of the trinitrate of $(-CH_2NH-)_3$ would be involved. This triazine has never been isolated, but it is thought to be an intermediate in the reaction of formaldehyde with ammonia to form hexamethylenetetramine (18), which is known to give 1 upon nitrolysis. Another possible route for the formation of 1 from 18 would of course involve direct nitronium ion attack, with expulsion of the neutral molecule CO_2.

Unlike the other approaches to 1 described herein, the nitrolysis of 19 would uniquely involve cleavage of an N→O bond. In addition to our standard nitrolysis procedures, we also employed treatment of 19 with liquid NO_2 (19), and with aqueous nitrous acid, by analogy to a known (1) procedures for generating the nitrimino group:

$$>NOH + HNO_2 \longrightarrow >NNO_2 + H_2O$$

None of these approaches yielded 1.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

The nitrolysis of the N-S bond is an established method for preparing nitramines in good yields from the N,N-dialkylsulfonamides of both aliphatic and aromatic sulfonic acids (6). In addition, 2 forms 1 in good yield, and, in fact, was seriously considered at one time for the production of 1 on a large scale. Compounds 20 and 21, however, gave no 1, which in the former case was noted by others (3).

We conclude from the above study that the preparation of 1 from 1,3,5-triacylhexahydro-s-triazines and related compounds is an approach limited, on the one hand, by the same steric and inductive factors already known to limit the preparation of nitramines from N,N-dialkylamides, and, in addition, by the lability of the triazine ring.

Detailed Study of Preferred Compounds 4 and 5

The good yields of 1 obtained from 4 and 5 in the preliminary tests summarized in Table I led us to make a more detailed study of their nitrolysis, the results of which are reported in Table II. It is noted that 5 always yields pure 1, while 4 always gives a mixture of 1 and TAX, except when using nitric acid-phosphorus pentoxide. This difficulty in removing the last alkanoyl group in the conversion of 4 to 1 was in fact unique among this group of compounds, since all of the others (5 – 9 inclusive) gave only pure 1. This much greater ease of removal of the propionyl vs. the acetyl group is especially noteworthy in the five-minute runs using nitric acid-trifluoroacetic anhydride, where the respective yields of 1 were 92 and 44%; the same was noted using nitric acid alone (55 and 15%). It is clear that 1 can be obtained from 4 or 5, by a suitable choice of conditions, in good to excellent yields, We have no explanation as yet for the high degree of variation in the yields of 1 from 5 when using nitric acid-polyphosphoric acid or nitric acid-sulfur trioxide.

Preliminary Economic Comparison

The overall process for preparing 1 via 4 or 5 would involve recovery of acetic or propionic acids and their recycle. One procedure for doing this involves the following Sequence A, with yields given parenthetically:

$$(1)\quad \underline{4} + 3\ HNO_3 \xrightarrow{PPA} \underline{1} + 3\ CH_3COOH \qquad (85\%)$$

$$(2)\quad 3\ CH_3COOH + 3\ NH_3 \longrightarrow 3\ CH_3CN + 6\ H_2O \qquad (94\%)$$

$$(3)\quad 3\ CH_3CN + 3\ CH_2O \longrightarrow \underline{4} \qquad (85\%)$$

Adding (1), (2), and (3), we have:

$$(4)\quad 3\ HNO_3 + 3\ NH_3 + 3\ CH_2O \longrightarrow \underline{1} + 6\ H_2O$$

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

Reaction (2) is well known (20). Reactions (1) and (3) were studied for us under contract (21): the later reaction is known (22).

A variation on the above is the following Sequence B;

$$(1)\quad \underline{4} + 3\ HNO_3 \xrightarrow{PPA} \underline{1} + 3\ CH_3COOH \qquad (85\%)$$

$$(5)\quad 3\ CH_3COOH + 3\ NH_3 \longrightarrow 3\ CH_3CONH_2 + 3\ H_2O \qquad (95\%)$$

Table II
Nitrolysis Studies of

$(-CH_2N(COCH_3)-)_3$ ($\underline{4}$), and $(-CH_2N(COC_2H_5)-)_3$ ($\underline{5}$)

Reagent	Reaction Conditions		Percent Crude Yield of $\underline{1}$ from	
	Minutes	Temp. (°C.)	$\underline{4}$[a]	$\underline{5}$[b]
$HNO_3-(F_3CCO)_2O$	60	50	87(96)	-
	30	50	87(92)[c]	98[c]
	5	50	58(76)	92
HNO_3 Alone	30	50	20(75)[c,d]	55[c]
$HNO_3-P_2O_5$	15	65	95[b,c,e]	80[c]
HNO_3-PPA[f]	15	70	87(98)[g]	74-93
$HNO_3-N_2O_5$	30	50	70(92)	92
HNO_3-SO_3[f]	120	27	-	40-93

[a] Parenthetical figures indicate the content of 1 in the crude, the remainder being TAX.

[b] Pure 1 in all cases.

[c] These data are from Table I.

[d] Ref. 21 noted 28–37% yields of crude 1, containing 16–24% TAX, using other conditions.

[e] Ref. 21 noted 67–83% yields of crude 1, containing 4–54% TAX, using other conditions.

[f] These experiments were run by Dr. R. W. Hutchinson of this laboratory; PPA = polyphosphoric acid.

[g] Ref. 21 noted 58–83% yields of crude 1 containing traces to 80% TAX, using other conditions.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

$$(6)\quad 3\ CH_3CONH_2 + 3\ CH_2O \longrightarrow \underline{4} + 3\ H_2O \qquad (85\%)$$

Adding (1), (5) and (6) again gives equation (4). Reaction (6) was improved from a low-yield to a high-yield process under a contract study (23); reaction (5) is known to proceed in good yield. It is noted that Sequences A and B differ in whether nitrile or amide is used as intermediate, and as to whether water removal is effected in two stages or one.

A third Sequence, C, is that now used to make $\underline{1}$ on a large scale:

$$(7)\quad 1/2\ (CH_2)_6N_4 + NH_4NO_3 + 2HNO_3 + 3(CH_3CO)_2O \longrightarrow \underline{1} + 6\ CH_3COOH \qquad (83\%)$$

$$(8)\quad 6\ CH_3COOH \longrightarrow 3\ (CH_3CO)_2O + 3\ H_2O \qquad (95\%)$$

$$(9)\quad 2\ NH_3 + 3\ CH_2O \longrightarrow 1/2\ (CH_2)_6N_4 + 3\ H_2O \qquad (95\%)$$

Adding (7), (8), and (9), again gives (4). In this case, the water is removed at two points and the recovered acetic acid is recycled as acetic anhydride.

It is therefore evident that in all three cases, we are merely using different overall expedients for reacting formaldehyde, ammonia, and nitric acid, and that which is the most economic method is determined by the efficiency of the intermediate reactions. Using available data, which for Sequences A and B are on a laboratory level, these three approaches have been subjected to a comparative cost analysis (24), with results summarized in Table III. It is noted that the two triazine procedures are closely similar in both Permanent Investment and Operating Cost, and that the Bachmann Process (Sequence C) has a somewhat higher Permanent Investment and a somewhat lower Operating Cost. Although it is felt that Operating Costs for all three procedures can be reduced somewhat with further study, it is concluded that the three methods are quite closely competitive.

Table III

RDX: Comparative Cost Data

Method	Permanent Investment	Operating Cost*
C (Bachmann)	1.00	1.00
A (Triazine via Nitrile)	0.83	1.15
B (Triazine via Amide)	0.83	1.15

* Includes raw materials, labor, utilities, and overhead.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

EXPERIMENTAL SECTION (25)

1,3,5-Triformylhexahydro-s-triazine, (3).

To acetic-formic anhydride (18.6 g.-0.21 mole), prepared by a published procedure (26) from acetic anhydride (21.4 g.-0.21 mole) and 98% formic acid (9.7g. -0.21 mole), was added portion-wise with stirring at 10° hexamethylenetetramine (6.7g. -0.048 mole). The viscous mixture was allowed to warm to room temperature over 2 hours with stirring to attain complete solution. Water (100 ml) was added slowly to destroy excess anhydride, followed by neutralization with solid potassium carbonate. The solution was evaporated to dryness in vacuo, and the residue was dried in vacuo over sodium hydroxide. It was then extracted with 3-250 ml. portions of chloroform. The combined extracts were filtered and evaporated, yielding 5.3g. (64%), m.p. 169.5-171°. Recrystallization from acetone-water raised the m.p. to 171-2°. NMR (deuteriochloroform): δ 5.32s (6H,CH_2); δ 8.20 s (3H,CHO).

Anal. Calcd, for $C_9H_9N_3O_3$: C,42.1;H,5.3;N,24.6. Found: C,42.2;H,5.3;N,24.3. Mol. wt.: Calcd.: 171. Found: 180 (osmometric), 171 (mass spectrometric) (27).

Triazines 7, 8, 9, and 15 were prepared from the corresponding nitriles and trioxane by a published procedure (28):

1,3,5-Tri(dimethylacetyl)hexahydro-s-triazine ,(8), was obtained in 45% crude yield; m.p. 150° (from 15% aqueous acetone); nmr (deuteriochloroform): δ 1.13d (18H,CH_3), J≈7cps; δ 3.03 sept. (3H,CH), J≈7cps; δ 5.33s (6H,CH_2). This compound was also prepared from the amide in 48% yield (23); an identical nmr spectrum was obtained.

Anal. Calcd. for $C_{15}H_{27}N_3O_3$:C,60.6;H,9.2. Found: C,60.9;H,9.3. Mol. wt. (osmometric): Calcd.: 297. Found: 297.

1,3,5-Tri(trimethylacetyl)hexahydro-s-triazine ,(9), 46% crude yield; m.p. 138-41° (from aqueous acetone); nmr (deuteriochloroform): δ 1.33s (27H,CH_3); δ 5.33s (6H,CH_2).

Anal. Calcd. for $C_{18}H_{33}N_3O_3$: C,63.7; H9.8. Found: C,63.3; H,10.1. Mol. wt. (osmometric): Calcd.: 339. Found: 316.

1,3,5-Triphenylacetylhexahydro-s-triazine,(15), 38% crude yield; m.p. 159-61° (from acetone); nmr (deuteriochloroform): δ 3.93s (6H,CH_2); δ 5.23s (6H, ring CH_2); δ 7.33s (15H,CH).

Anal. Calcd. for $C_{27}H_{27}N_3O_3$: N,9.5. Found: n,9.9. Mol. wt. (osmometric): Calcd.: 441. Found: 436.

1,3,5-Tri-n-hexanoylhexahydro-s-triazine,(7), was obtained in 80% yield as a viscous oil which would not be crystallized. Nmr (deuteriochloroform): δ 0.90t (9H,CH_3), J≅7 cps; δ 1.17-1.90m [18H,$(CH_2)_3$]; δ 2.53t (6 H, $COCH_2$), J≅7 cps; δ 5.30s (6H,CH_2). Mol. wt. (osmometric): Calcd: 381. Found 374. This compound was also prepared from the amide in 85% yield (23); an identical nmr spectrum was obtained.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

1,3,5-Tri(methoxyacetyl)hexahydro-s-triazine ,(11).

A solution of 1.7g (0.03 mole) potassium hydroxide in 25 ml. absolute methanol was added to 3.2g. (0.01 mole) of 10 suspended in 100 ml. of the same solvent. After refluxing 21 hours, the mixture was filtered, and the filtrate was evaporated to an oily slurry, which was extracted with chloroform. The solvent was evaporated, yielding 3.4g of a yellow oil. It could not be purified, and was therefore used as such, since nmr analysis showed it to comprise mainly 11 (nmr(deuteriochloroform): δ 5.32 (s, 6H, ring CH_2), δ 4.50 (s, 6H, CH_2), δ 3.46 (s, 9H,CH3)) plus some N,N-methylene-bis-methoxyacetamide (nmr(deuteriochloroform): δ 7.46 (broad t, 2H,NH), δ 4.75 (t, J=6Hz , 2H, N-CH_2N), δ 3.92 (s, 4H, CH_2), δ 3.43 (s, 6H, CH_3)), and an unidentified impurity.

1,3,5-Tricarboxyhexahydro-s-triazine, tripotassium salt ,(18).

Compound 16 (4.4 g. - 0.017 mole), potassium hydroxide pellets (4.2 g. -0.075 mole (50% excess)), and methanol (100 ml.) were mixed and stirred at room temperature for 24 hours. The slurry was evaporated to dryness over 6 hours at 50°; yield 7.3g. white solid. The same material was also prepared from 17; efforts to purify it were unsuccessful. It dissolves easily in water. The solution evolves carbon dioxide upon acidification, and ammonia upon boiling with aqueous base. Nmr (D_2O): δ 4.73 s.

Anal. (on the crude). Calcd. for $C_6H_6K_3N_3O_6 \cdot 1\ H_2O$: C, 20.4; H, 2.3; K, 33.2; N, 11.8. Found: C,19.4; H, 2.3; K, 33.1; N, 11.2.

1,3,5-Triacetoxyhexahydro-s-triazine, (20).

The following procedure was found superior to those (29, 30) reported in the literature. An aqueous solution of formaldoxime was prepared by a published procedure ,(31), using hydroxylamine (35.0 g.-0.5 mole), paraformaldehyde (18 g. of 90% purity -0.54 mole), anhydrous sodium acetate (41.0g. -0.5 mole) and 200 ml. water. The reagents were mixed and refluxed for 15 minutes. The solution was cooled and extracted with 4-150 ml. portions of ethyl ether. The combined extracts were dried by shaking with anhydrous sodium sulfate, and refluxed 1 hour with acetic anhydride (26.0 g. -0.5 mole). The solvent and excess anhydride were removed in vacuo, giving a viscous syrup which solidified upon trituration with cold butanol. The crystals were filtered and dried. The yield was 8.7 g. (20%), m.p. 132° (lit. 132° ,(30),. Nmr (deuteriochloroform): δ 2.13 s (9 H,CH_3), δ 4.60 s (6 H,CH_2).

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

1-Acetyl-3,5-dinitrohexahydro-s-triazine ("TAX").

The following preparative procedure is superior to those described in the literature (32, 33, 34), in which it was isolated in low yield from mixtures with related compounds. Compound 4 (1.4 g. -0.007 mole) and trifluoroacetic anhydride 15.2 g. -0.073 mole) were mixed at 15° in a flask equipped with magnetic stirrer, dropping funnel, and external cooling bath. Nitric acid (3.0 g. of 99% acid -0.048 mole) was added dropwise with stirring and cooling at 15-20°. The cooling bath was removed and stirring was continued. After about 10 minutes, the temperature began to rise slowly and a solid began to precipitate. The temperature was held at 30-40° by periodic application of the cooling bath. When the exothermic reaction ceased, the mixture was stirred for a few minutes, for a total reaction time of about 1 hour. The reaction mixture was mixed with cold water, and the solid product was filtered and dried. The yield was 1.3g. (93% of theory), m.p. 140-50°. Two recrystallizations from isopropanol gave m.p. 148-52° (lit. 153-5° (32). Nmr (acetone-d_6): δ 6.25 (s, 2H, $(O_2NN)_2CH_2$), δ 5.80 (s, 4H, remaining CH_2), δ 2.27 (s, 3H, CH_3). Ir (potassium bromide), 3060, 1660 (CH_3CON), 1580 (O_2NN), 1420, 1370, 1280 (O_2NN), 1240, 1180, 1030, 990, 920, 880, 850, 810, 750, 630, 585, and 490 cm^{-1}.

Nitrolysis Procedures

Nitric Acid-Phosphorus Pentoxide. To phosphorus pentoxide (10.0 g. -0.070 mole) in a 100 ml. three-necked flask, equipped with thermometer, magnetic stirrer, and reflux condenser, is added all at once with stirring at room temperature 99% nitric acid (30.0 g. -0.480 mole (20 ml.). No external cooling is used, and an exotherm occurs, taking the reaction temperature to about 60°. After cooling to 35°, 1.0 g. of the organic compound (0.018 mole or less of amido group), is added rapidly with stirring. The mixture is then heated rapidly to 65° and held there for 15 minutes, after which it was quenched on ice and the product filtered and dried.

The purity of the 1 obtained was established by melting behavior, and by ir and nmr spectral data. Highly purified 1 melts at 204.5° (dec.) (34). Ir (potassium bromide): 3060, 3000, 1570 (O_2NN), 1525, 1455, 1420, 1380, 1350, 1310, 1260 (O_2NN), 1220, 1035, 910, 880, 840, 780, 750, 670, 590, 460, 410, and 340 cm-1. The presence of TAX as an impurity was detected by the CH_3CON peak at 1660 cm^{-1}. The quantity of TAX in crude 1 was determined by relative nmr peak heights. Others (21) have reported the occasional formation of some by-product 1,3-diacetyl-5-nitrohexahydro-s-triazine from the nitrolysis of 4. It was noted only when TAX formation was high, the quantity usually being < 10% by weight of the TAX. We encountered none of this material in our work. Nmr data for it (<u>21</u>) are as follows: (DMSO-d_6): δ 2.17 (s, 6H, $2CH_3$), δ 5.27 (s, 2H,AcN-$\underline{CH_2}$ -NAc), δ 5.70 (s, 4H, -CH_2N (NO_2) CH_2-).

Nitric Acid. The compound (1.0g. -0.018 mole or less of amido group) is added quickly to 99% nitric acid (30.0g. -0.480 mole -20ml.) at room temperature in a flask equipped with a thermometer and magnetic stirrer. The flask is then immersed in a water bath preheated to 70°, and the reaction mixture is held at this temperature for 15 minutes. The solution is then quenched on ice, and the product is filtered and dried.

Nitric Acid-Trifluoroacetic Anhydride. To 99% nitric acid (15.0 g. -234 mole -10 ml.) is added dropwise at 5-10°, with cooling and stirring, trifluoroacetic anhydride (10.0g. -0.048 mole -6.5 ml.). The organic compound (1.0g.) is added all at once, and the flask is then immersed in a water bath preheated to 50°. The mixture is held at this temperature for 30 minutes, and is then quenched in ice water to precipitate the product, which is filtered and dried.

Nitrations of <u>4</u> and <u>5</u> with polyphosphoric acid were done at 70° for 15 minutes using 5.0g. compound (corresponding to 0.071 and 0.059 mole amido group, respectively), 9.0 g. (0.140 mole) 99% nitric acid and 10.0 g. polyphosphoric acid (83% P_2O_5). The nitration of <u>5</u> with sulfur trioxide was effected at 27° for 2 hours, using 3.0 g. (0.035 mole amido group), 30.0 g. (0.470 mole) 99% nitric acid and 7.2 g. (0.090 mole) liquid sulfur trioxide; the acids were carefully premixed at 5°.

ABSTRACT

Nineteen triazines, $(-CH_2N(R)-)_3$, were nitrolyzed by several procedures for preparation of the explosive RDX ($R=NO_2$). The reaction succeeds only when R is alkanoyl or KOCO. With R = acetyl, mixtures of RDX and the monoacetyldinitro analogue (TAX) were usually formed; in all other cases, the product was pure RDX. Nitric acid-trifluoroacetic anhydride gave the best yields (max. 98%), followed successively by nitric acid -P_2O_5 (80%), and nitric acid alone (55%). Three other nitrolysis systems were considered briefly. A preliminary economic comparison of the triazine process with the current Bachmann process, which uses hexamethylenetetramine and acetic anhydride, shows that the former method entails lower plant investment and higher operating cost than the latter. Further improvements appear possible with both procedures.

LITERATURE CITED

(1) G.F.Wright, "Methods of Formation of the Nitramine Group, Its Properties and Reactions", in The Chemistry of the Nitro and Nitroso Groups", Part 1, H.Feuer, Ed., Interscience, New York, 1969, pg. 613 ff.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

(2) A.T.Blomquist, OSRD Report 4134 (1944), pg. 135-6.
(3) G.C.Bassler, "The Chemistry of Cyclonite", PhD Thesis, Pennsylvania State University, 1943.
(4) D.N.Thatcher, U.S. Patent 3,178,430 (1965).
(5) M.Warman, V.I.Siele, E.E.Gilbert, J.Het. Chem. 10, 97 (1973)
(6) J.H.Robson, J.Reinhart, J.Am.Chem. Soc. 77, 2453 (1955).
(7) J.H.Robson, J.Am.Chem. Soc. 77,107 (1955).
(8) M.B.Frankel, C.H.Tieman, C.R.Vanneman, M.H.Gold, J.Org. Chem. 25, 744 (1960).
(9) This procedure was developed by Mr. V.I.Siele of this laboratory.
(10) H.A.Levine, U.S. Patent 2,976,152 (1961).
(11) E.M.Smolin, L.Rapoport, "s-Triazines and Derivatives", Interscience Publishers, New York, 1959, pg. 533.
(12) M.A.Gradsten, M.W.Pollock, J.Am.Chem. Soc. 70, 3079 (1948).
(13) R.Wegler, A.Ballauf, Chem. Ber. 81, 527 (1948).
(14) B.S.Thyagarajan, K.C.Majumdar, J.Het. Chem. 11,937 (1974).
(15) E.E.Gilbert, Int. J. Sulfur Chem. 3(1), 43 (1973).
(16) V.Grakauskas, K.Baum, J.Org.Chem. 37 (2), 334 (1972).
(17) A.P.N.Franchimont, Rec. Trav. Chim. 3, 216 (1884).
(18) Y.Ogata, A.Kawasaki, in "The Chemistry of the Carbonyl Group", Vol. 2, J.Zabicky, Ed., Interscience, New York, 1970, pg. 51.
(19) Private communication, Professor B.S.Thyagarajan, University of Idaho.
(20) E.L.Tollefson, R.M.Dicker, C.B.Johnson, Can.J.Eng. 48, 219 (1970).
(21) E.I.duPont de Nemours & Co., Dr. C.H.Rolston, Principal Investigator, Contract No. DAAA-21-71-C-0542.
(22) M.A.Gradsten, M.W.Pollock, J.Am.Chem. Soc. 70, 3079 (1948).
(23) Stanford Research Institute, Dr. C.L.Coon, Principal Investigator, Contract No. DAAA-21-73-C-0487.
(24) Stanford Research Institute, Dr. Y.C.Yen, Process Economics Group, Contract No. as in Ref. 23.
(25) Melting points were taken in capillary tubes in a Thomas-Hoover apparatus, and are uncorrected. Infrared spectra were determined in potassium bromide pellets with a Perkin-Elmer Model 457 A spectrophotometer. Nmr spectra were determined in the stated solvent on a Varian T-60 spectrometer, using tetramethylsilane as internal reference. Microanalyses and molecular weights were run by Schwarzkopf Microanalytical laboratory, Woodside, N.Y.
(26) L.F.Fieser, M.Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, pg. 4.
(27) We are indebted to Professor T.Axenrod, City University of New York, for this determination.
(28) W.Emmons, H.Rolewicz, W.Cannon, R.Ross, J.Am.Chem.Soc. 74, 5524 (1952).
(29) W.R.Dunstan, A.L.Bossi, J.Chem. Soc. 73, 353 (1898).
(30) H. Kraessig, H.Ringsdorf, Macromol, Chem. 22, 163 (1957).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

(31) S.D.Jolad, S.Rajagopal, Org. Syn. Coll. Vol. V, H.E.Baumgarten, Ed., Wiley, New York, 1973, pg. 139.

(32) W.J.Chute, A.F.McKay, R.H.Mean, G.S.Myers, G.F.Wright, Can. J.Res. 27B, 503 (1949).

(33) K.W.Dunning, W.J.Dunning, J.Chem Soc. 1950, 2920.

(34) F.Chapman, P.G.Owston, D.Woodcock, J.Chem.Soc. 1949, 1638.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch023

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch024

24

Safe Manufacture and Handling of Nitric Esters: The Injector Nitration Process

B. BRUNNBERG

Nitro Nobel AB, S-710 30 Gyttorp, Sweden

During the nitration of aliphatic alcohols such as glycerol and glycol a certain amount of heat is developed. This is sufficient to start decomposition of the nitrated product, adding further heat to the mixture and accelerating decomposition, forming oxidation products. For this reason all older nitration processes, continuous as well as batchwise, were performed in reaction vessels provided with cooling coils. A good contact between the reacting liquid and the surface of the cooling coils was of very great importance.

However, there is another way to overcome this problem. This method was demonstrated as early as 1904 by Dynamit AG, previously Nobel & Co. (GP 195231) with a process using not fresh nitrating acid but a portion of spent acid from the previous operation, revivified to the original composition. For the revivification, however, high strength oleum was necessary, and it was preferable to use oleum at the start to produce a highly concentrated nitrating acid and so obtain better results. For this reason the patented process found no practical application.

Without knowledge of this method, Agne Nilsson at Nitro Nobel Co., earlier Nitroglycerin AB, in about 1950 started nitration trials of glycerol and glycol with such revivified acids. For mixing the alcohols and the nitrating acid he used an injector, passing the nitrating acid, which is the main part of the liquids, through the injector nozzle and adding the alcohol to the throat, where the two components were mixed very rapidly and intensively. Among many results of interest from these trials, he found that he could partly control the nitration temperature by varying the amount of spent acid in the revivified nitrating acid and also that considerably higher nitration temperature can be used - over 60°C - without starting any decomposition or oxidizing reactions. The process was patented in many countries but never built on a full scale. The main reason was the problem involved in static separation of the acid nitrate ester from a great quantity of spent acid.

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

In 1954 Bernt Brunnberg, also of Nitro Nobel Co., started trials with centrifugal separation of nitroglycerine and nitroglycol from spent acid. He found the most convenient centrifugal force to get a good and safe separation without having too much sludge (ferrosulfate) from the acid to separate and block the channels in the centrifuge. He also assisted in the development of one of these delicate separation machines.

Regarding the injector nitration process, he modified the method in such a way that the vacuum created by the acid flow through the injector nozzle was used to suck in the correct amount of alcohol. The intention was to make the process as safe as possible, preventing any dosage of alcohol without a sufficient quantity of nitrating acid running through the injector.

This method, together with the centrifugal separation, formed the basis of a second injector nitration patent, according to which the process has been built and used in many factories around the world. The following is a very short description of the process.

Strong mixed acid is normally made of highly concentrated nitric acid and 20% oleum. One part of this acid is mixed with 1.6 parts of spent acid, forming a nitrating acid with about 27% nitric acid. It is pumped to the injector via a cooler, where it is cooled down to 0°C. This temperature is thermostatically regulated. In the injector the acid flow creates a vacuum which is regulated to about 250mm Hg. Warmed glycerol or glycol can be sucked into the injector and the correct quantity of the alcohol gives a temperature raise of 46-48°C. The reaction is almost instantaneous because of the very good mixing efficiency of the injector. In all modern installations the influx of alcohol is automatically regulated and registered. Only one second after the two components are mixed, cooling of the emulsion starts, first in a coil with cold water or brine and thereafter in a tubular cooler with brine cooling. The final temperature of the emulsion is about +15°C. The emulsion runs by gravity to a separately placed centrifuge. The quantity of free and potentially explosive nitric ester in the rotating bowl is 4 or 8kgs, depending on the size of the centrifuge. The spent acid containing max 0.1% emulsified nitric ester runs either to a tank for preparation of new nitrating acid or to pumps for transport to the denitration plant. Before pumping, the acid is normally mixed with 4-5% water.

The acid nitric ester from the centrifuge runs to an injector where it is mixed with 8% soda water. It is transported to a special degassing vessel, where carbon dioxide is separated and excess of soda water is controlled by pH-metering. Thereafter, the emulsion passes to two wash columns provided with perforated discs, all made of stainless steel. Mixing and transport takes place by air inlet to the columns. From the second column the emulsion runs to a specially designed wash

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch024

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch024

centrifuge, from where the separated wash liquid runs through a catch tank to discharge. The stabilized nitric ester runs to an injector and is normally transported as a non-explosive water emulsion to a separate storage building.

Regarding safety aspects of the injector nitration process, the most remarkable feature to notice is the very small quantity of the nitric esters present in the reaction space and the very short time of reaction. This is only about one second and there is never enough nitric esters in the reaction zone to damage the injector if an explosion should occur. After the reaction is finished, the content of nitric ester in the acid is too small to make it explosive, e.g. it cannot be initiated by a detonator. Nor can the nitric ester separate in the nitration apparatus. If the nitration is stopped for any reason, the emulsion is flowing down, leaving the apparatus empty and normally cleaned by pure nitrating acid. Thus, there is no need for a safety tank for drowning of nitric esters and acids in case of emergency.

If the power fails or the reaction temperature becomes too high, a valve for inlet of air to the injector automatically opens, which instantaneously prevents any more alcohol being sucked into the injector. If the electric current returns, the nitration process cannot start by itself.

Centrifugal separation of nitric esters can be considered extremely safe and reliable in operation, provided that lubrication and other servicing of the centrifuge is carried out according to the instructions. During nitration the centrifuge does not contain enough quanitity of nitric esters to cause damage outside the room in which the separation takes place.

The injector nitration process is remotely supervised from a control room, where the personnel work in complete safety.

25

Effect of Gamma Radiation on Vapor Phase Nitration of Propane

ROBERTO LEE,[1] TAE CHUNG,[2] and LYLE F. ALBRIGHT

Purdue University, West Lafayette, Ind. 47907

[1] Present address: Monsanto Company, St. Louis, Mo.
[2] Present address: Upjohn Co., North Haven, Conn.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch025

Gamma radiation has been found to affect the kinetics and the course of several chemical reactions (1-6). Beneficial effects are frequently obtained for free-radical reactions. The present investigation was made to determine the effects of radiation on vapor-phase nitration.

The following mechanism is generally considered to be predominant when propane is nitrated (7-9):

$$HNO_3 \rightarrow HO\cdot + \cdot NO_2$$

$$C_3H_8 + HO\cdot \rightarrow C_3H_7\cdot + H_2O$$

$$C_3H_7\cdot + HONO_2 \rightarrow C_3H_7NO_2 + HO\cdot$$

During the nitration reaction, oxidation steps also occur and C-C bonds are broken. Products obtained include nitromethane (NM), nitroethane (NE), 1-nitropropane (1-NP), 2-nitropropane (2-NP), aldehydes, other oxygenated products, olefins, carbon dioxide, carbon monoxide, and water (10-13). The approximate ranges of the operating variables reported (7-14) for the process include temperatures from 370 to 450°C, pressures from atmospheric up to about 200 psi, and contact times from 0.5 to 4.0 sec. The mole ratios of propane to nitric acid have ranged from 1:1 in a salt bath reactor (14) to 20:1 in commercial nitrators (7). Several additives (oxygen, chlorine, bromine, and ozone) which apparently promote free radical formation have been found to improve conversion and alter product distribution (11-13).

Experimental Details

The stainless-steel flow reactor used was similar to the one employed by Liebenthal et al. (3) for the partial oxidation of propane. It was heated electrically, as were the inlet and outlet lines to the reactor to prevent condensation. The

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Cobalt-60 source used provided a gamma radiation intensity of about 195,000 roentgens per hour. The reactor could be inserted inside the Co-60 source for irradiated runs. Alternatively, gaseous or liquid propane was sometimes irradiated in a stainless-steel cell prior to the nitration step. The exposure time was generally about 3 seconds for the gaseous propane and 40 to 50 hours for the liquid.

The flow sheet for the equipment and the product recovery procedure resembled those employed by Albright et al. (9). In runs involving oxygen and chlorine, the reagent was introduced to the gaseous mixture of propane and nitric acid just before the reactants entered the reactor. The entering mixture was maintained in all runs at about 120-150°C.

The feed materials used were as follows: propane 99 + % purity, oxygen 99 + % purity, and nitric acid 70 weight %.

Results

Eleven sets of nitration experiments, consisting of 58 runs, were made. The operating conditions and pertinent results are summarized in Table I. Propane did not nitrate at temperatures below 370°C with or without gamma radiation. Above 460°C excessive decomposition occurred. The nitric acid conversions and nitroparaffin product distributions in general correlate well with the average reactor temperature which was determined using four thermocouples positioned at various heights in the reactor thermowell. This average reactor temperature was also utilized to calculate the contact time.

Without additives, both unirradiated and irradiated runs had optimum nitric acid conversions of 27-28% at 425-430°C. These series of runs were made using propane-to-nitric acid ratios of 6:1 and 10:1. Irradiation of propane gas prior to its introduction to the reactor did not significantly increase conversion. When liquid propane was irradiated for 40-50 hours and the resulting propane was nitrated, nitric acid conversions increased to 31%.

In terms of product distribution, the relative amounts of NM and NE were quite low as indicated by the relatively high molecular weight of the nitroparaffin products, as shown in Table I. The amounts of 1-NP increased and 2-NP decreased with temperature increases; each of these compounds occurred in relatively large quantities. Gamma radiation did not change nitroparaffin product distribution appreciably, but somewhat more scattering of data occurred. The average molecular weight of nitroparaffins in all cases tended to decrease slightly as the temperature increased.

Nitration reactions "catalyzed" with oxygen at an oxygen-to-nitric acid ratio of 1.05, produced the following results:

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch025

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch025

Table I Summary of Nitration Runs

	No. of Runs	Contact Time, Sec	Av. Mole Ratio of Propane to Nitric Acid	Temp. Range, °C	HNO_3 Conversion Range, %	Average Molecular Weight of Nitroparaffins*
I. Nitration without Additives						
1. Unirradiated Reactor	4	1.1	10.1	409-439	15.9-26.9	82.5-83.3
2. Unirradiated Reactor	9	1.2	6.4	398-451	4.4-27.2	78.6-84.6
3. Irradiated Reactor	6	1.1	10.9	408-449	13.7-27.4	82.9-83.2
4. Irradiated Reactor	6	1.2	6.2	413-441	14.0-31.1	81.6-83.0
5. Irradiated Propane Gas	3	1.9	15.9	423-436	27.4-28.3	82.2-86.6
6. Irradiated Liquid Propane	7	1.5	8.5	400-449	11.5-30.8	83.5-87.8
7. Irradiated Liquid Propane	3	1.2	4.1	412-433	28.3-30.9	79.6-83.1

*The molecular weights of nitropropanes, nitroethane, and nitromethane are 89, 75, and 61 respectively

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch025

Table I Summary of Nitration Runs (cont.)

	No. of Runs	Contact Time, Sec.	Av. Mole Ratio of Propane to Nitric Acid	Av. Mole Ratio of Additive Of Nitric Acid	Temp. Range, °C	HNO_3 Conversion Range, %	Average Molecular Weight of Nitroparaffins
II. Nitration with Oxygen							
1. Unirradiated Reactor	5	1.1	10.9	1.05	377-440	26.9-36.6	76.5-82.5
2. Irradiated Reactor	8	1.1	11.1	1.07	387-459	21.6-39.4	77.0-78.2
III. Nitration with Chlorine							
1. Unirradiated Reactor	3	1.2	14.2	0.24	416-452	19.8-22.7	84.8-85.5
2. Irradiated Reactor	4	1.2	13.0	0.22	417-450	18.0-22.1	84.3-85.8

1. The optimum conversion for the unirradiated series of runs was 36.6% at about 400°C. The corresponding optimum conversion for the irradiated runs was about 39.4% at 420°C.
2. Gamma radiation had little or no effect on product composition.

Chlorine was used as an additive in a series of runs with residence times of about 1.2 seconds and a ratio of propane-to-nitric acid of 13.5. The mole ratio of chlorine to nitric acid was 0.2. Chlorine tended to lower nitric acid conversions, suppress C-C bond breakage, and promote 2-NP formation. The maximum conversion was about 23% for both irradiated and unirradiated runs. Gamma radiation had little effect on either nitric acid conversions or product composition.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch025

Discussion of Results and Conclusions

The reason why irradiation caused relatively small but nevertheless significant increases of nitric acid conversions in some cases but had little or no effect in others is not known. The small amounts of hydrogen, methane, ethane detected after liquid propane was irradiated are not thought to be beneficial in improving nitric acid conversions. Of interest, irradiation increases the rates of oxidation of both hydrogen and paraffins (4,5); these results combined with the results of the present investigation suggest that radiation activates in some manner oxygen. It was surprising that irradiation did not increase nitric acid conversions when chlorine was used as an additive; chlorination reactions are often significantly affected by radiation (2,3). Clearly more information is still needed to explain the results of the present investigation.

Abstract

Propane was nitrated with nitric acid in a tubular flow reactor which could be subjected to 195,000 roentgens per hour of gamma radiation from a Cobalt-60 source. The reaction was investigated at operating conditions of commercial interest. Irradiation of the reacting mixture had little effect on the nitric acid conversion, except when oxygen was added to the reactants or when liquid propane was irradiated prior to reaction. Under these conditions, a 10 to 15% relative increase was noted. The product distribution was unaffected by radiation.

Literature Cited

1. Crean, L.E., Mins, L.S., and Martin, J.J., Chem. Eng. Prog., 56, 73 (Oct., 1960).
2. Harmer, O.E., Anderson, L.C., and Martin, J.J., Chem. Eng. Prog. Symposium Series 50, No. 11, 253 (1954).
3. Liebenthal, J.L., Albright, L.F., and Sesonske, A., Proceedings of Second United Nations International Conference on Peaceful Use of Atomic Energy, 29, 107 (1959).
4. Martin, J.J., Chem. Eng. Prog. 54, No. 2, 66 (1958).
5. Nield, L.A. and Albright, L.F., Journal Chem. Eng. Data 10, 275 (1965).
6. Royals, E.E., "Advanced Organic Chemistry", Prentice-Hall, New Jersey (1958).
7. Albright, L.F., Chemical Engineering 73, 12, 149 (1966).
8. Albright, L.F., Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Vol. 13, pp. 784-796 (1967).
9. Albright, L.F., Locke, S.A., MacFarlane, D.R., and Glahn, G.L. Ind. Eng. Chem., 52, 221 (1960).
10. Bachman, G.B., Addison, L.M., Hewett, J.V., Kohn, L., and Millikan, A., J. Org. Chem., 17, 906-13 (1952).
11. Bachman, G.B., Atwood, M.T., and Pollack, M., J. Org. Chem., 19, 312-323 (1954).
12. Bachman, G.B., Hewett, J.W., and Millikan, A.G., J. Org. Chem. 17, 942-54 (1952).
13. Bachman, G.B. and Standish, N.W., J. Org. Chem., 26, 570 (1961).
14. Coldiron, D.C., Albright, L.F., and Alexander, L.G., Ind. Eng. Chem., 50, 991 (1958).

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ch025

INDEX

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ix001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ix001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ix001

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ix001

In Industrial and Laboratory Nitrations; Albright, L., el al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1976.

Publication Date: June 1, 1976 | doi: 10.1021/bk-1976-0022.ix001