

Table VI. Glc Data for Separation of Alcohols

Ketone	Column oven temp, °C	Retention time, min	
		Axial alcohol ^a	Equatorial alcohol
2	84	19.8	21.9
3	114	10.8	12.7
4	120	19.4	21.9
<i>cis</i> -6	108	7.6	8.8
<i>trans</i> -6	108		11.8
7	116	13.8	18.1
8	125	11.6	16.2
9	118	13.2	15.7

^a *I.e.*, cis to the group at the 2 position.

aliquot was then injected into the gas chromatograph. This proved a convenient amount to make the largest peak cause full-scale deflection of the chart pen and to be able to see the smallest peaks.

3,3-Dimethyl-6-Isopropylcyclohexanone (8). To a stirred suspension of copper(I) iodide (20.1 g, 0.106 mol) in anhydrous ether (450 ml) under nitrogen and in an ice bath was added a 1.75 M solution of methylolithium (88 ml, 0.154 mol) in ether. The suspension was stirred at 0° until a tan color appeared (5 min). Piperitone (5.04 g, 0.033 mol) in anhydrous ether (125 ml) was added dropwise over 25 min. The reaction mixture was allowed to stir at 0° for 2 hr and then poured with stirring into 1 N HCl (1 l.). The mixture was filtered by suction to remove the inorganic pre-

cipitate and the aqueous filtrate extracted with ether (10 × 100 ml). The combined extracts were dried (brine; Na₂SO₄) and ether was removed by rotary evaporation to give a yellow liquid (5.22 g; 94%). Glc analysis showed the absence of starting ketone, but the presence of a major impurity (37%). Column chromatography (silica gel, petroleum ether) gave 3.0 g of material (90% purity) which was rechromatographed (silica gel, petroleum ether; petroleum ether-benzene (1:1)) to afford ketone in a purity of greater than 99%: δ 0.90 (6 H, d, $J = 6$ Hz), 0.90 (3 H, s), 1.02 (3 H, s), 1.17 (1 H, m), 1.60 (2 H, m), 1.80 (2 H, m), 2.02 (2 H, s); ν_{\max} 1710 cm⁻¹ (carbonyl); m/e 168, 153, 126, 111, 98, 83. *Anal.* Calcd for C₁₁H₂₀O: C, 78.55; H, 11.86. Found: C, 78.51; H, 11.98. Simultaneous injection with a sample kindly supplied by Professor G. Stork showed identity of retention times of the two samples.

Menthone was prepared by the Brown oxidation of menthol,¹⁴ bp 101° (12 mm) (lit.¹⁴ 66.7° (4 mm)), n_D^{20} 1.4497 (lit.¹⁴ 1.4500).

2-*n*-Butylcyclohexanone was prepared from a mixture of the corresponding alcohols by Brown oxidation,¹⁴ bp 105–106° (15 mm) (lit.²⁴ 93.5° (11 mm)), n_D^{20} 1.4528 (lit.²⁴ 1.4548).

2-*tert*-Butylcyclohexanone was prepared by ochromate oxidation²⁵ of commercial verdol in 87% yield, bp 136–138° (20 mm) (lit.²⁶ 80–82° (13 mm)), n_D^{20} 1.4565 (lit.²⁶ 1.4561).

Acknowledgments. It is a pleasure to acknowledge some most helpful correspondence with Professors E. L. Eliel and Bruce Rickborn.

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Aromatic Substitution. XXXIV.¹ The Differing Nature and Selectivity of the Nitration of Nitro(dinitro)benzene and -toluenes from that of Benzene and Toluene

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Abstract: The competitive and noncompetitive rates and isomer distributions of nitration of nitro(dinitro)benzene and -toluenes with nitronium salts in nitromethane and sulfuric acid solutions were determined. The reactions show high substrate selectivity indicating "late," *i.e.*, arenium ion like nature of the transition states of highest energy. This is also reflected in the increased para substitutions (related to the methyl group) in nitration of nitro-toluenes. The significant differences in the nature and selectivity of the nitronium salt nitration of benzene and toluene from those of nitro(dinitro)benzene and -toluenes are discussed in terms of the differing nature of the involved transition states.

Electrophilic nitration has been one of the most widely studied electrophilic aromatic substitution reactions and was extensively reviewed.^{2–8}

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The idea that the actual nitrating agent in aromatic nitration might be the nitronium ion, NO₂⁺, was suggested by von Euler⁹ as early as 1903 and has since then been supported by numerous authors,^{10–12} most notably by Ingold.¹³

Stable nitronium salts were introduced as nitrating agents in our work^{14,15} in 1956. They were found useful both in preparative nitration¹⁶ and in the investi-

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gation of mechanistic aspects of aromatic nitration.¹⁷⁻²¹ In the course of these investigations, the competitive nitration of benzene and toluene, as well as other aromatics, was carried out in organic solvents.

Under usual conditions of electrophilic nitration, toluene reacts about 20 times more rapidly than benzene. With nitronium salts toluene reacts about as fast as benzene.¹⁷ The disappearance of the intermolecular (substrate) selectivity was accompanied by no significant alteration of isomer distribution (positional selectivity). This observation led to the suggestion that the transition state of highest energy (which determines substrate selectivity) is of a π -complex nature, which is then followed by σ -complex formation, determining positional selectivity. The π -complex type transition states have been termed as "early" transition states (lying early on the reaction coordinate of the potential energy diagram) in comparison with the "late" transition states resembling the Wheland intermediate (σ complex).

Our concepts were criticized,²² primarily on the basis that the nitronium salt reagents used were too reactive to allow real differentiation under competitive reaction conditions and low substrate selectivity could be a consequence of the fast reactions before uniform mixing of the reagents was achieved. It was suggested that the nitration of reactive alkylbenzenes takes place under conditions of encounter and not kinetic reaction control. Indeed the nitration of toluene and benzene, for example, are too fast for their noncompetitive rates to be measured, even with stopped flow techniques.

Encounter control could explain low substrate selectivity in aromatic substitutions, but would not account for simultaneous changes of substrate and positional selectivity.

In a series of recent studies we have proved²³ that the transition states of electrophilic aromatic substitution are not rigidly fixed, but can shift from "early" to "late" depending on the reactivity of electrophiles and the basicity of aromatic substrates. In these reactions a regular shift of substrate and positional selectivities was always observed. Low selectivity reactions generally show low substrate selectivity (as generally expressed by $k_T:k_B$ rate ratios) with usually *high* ortho/para isomer ratios (the meta isomer generally staying low, 2-5%). High selectivity is reflected by high $k_T:k_B$ rate ratios and generally *low* ortho/para isomer ratios, the amount of meta isomer, however, being very low (only 1-2%). In most of these studies noncompetitive rates could also

be determined, excluding encounter controlled reactions.

In electrophilic nitration the nature of the nitrating agent cannot be readily changed although there exists the possibility that certain precursors of the nitronium ion, such as acetyl nitrate or nitril halide-Lewis acid complexes, can be nitrating agents in their own right.⁵

Electrophilic nitrations of toluene and benzene show little change in positional selectivity (isomer distribution), although somewhat more differentiation in substrate selectivity. As discussed, the low k_T/k_B values and high ortho/para isomer ratios indicate early transition states of highest energy of π complex or benzenonium ion nature.

Not only the electrophilicity of the reagent but also the nucleophilicity of the aromatic substrate can affect the relative position and heights of the involved transition states. Whereas nitrations cannot be widely 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 can be demonstrated in comparing nitration of nitrobenzene and nitrotoluenes. These studies also allow the determination of noncompetitive reaction rates, thus excluding any question of encounter control.

Results and Discussion

Since the pioneering work of Martinsen,^{24,25} the kinetics of the nitration of aromatic nitro compounds have been studied in detail. These studies include use of nitric acid in different solvents,²⁶⁻³⁴ and the more recent work of Ciaccio and Marcus,³⁴ and Kilpatrick, Kilpatrick, and Jones³⁵ using nitronium tetrafluoroborate in several solvents.

In the above studies, the rates of nitration have been shown to be first order in nitro compounds, and are much slower than the nitration rates of benzene and toluene.³⁶ This is due to the fact that introduction of nitro groups deactivates the ring thus making it less susceptible to attack by the nitrating agent.

Competitive nitrations of nitrobenzene and nitrotoluenes are slow, thus cannot be affected by any diffusion control and allow us to study the substituent effect of a methyl group compared to the H atom in electrophilic nitration of a deactivated systems. We now report the competitive nitration of nitrobenzene

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and nitrotoluenes with nitronium hexafluorophosphate in both nitromethane and 96% H₂SO₄ solution at 25°. The results are shown in Table I.

Table I. Competitive Nitration of Nitrotoluenes and Nitrobenzene with NO₂⁺PF₆⁻ at 25°

ArH	k_{NT}/k_{NB}^a	Isomer distribution, %				
		2,3-	2,4-	2,5-	2,6-	3,4-, 3,5-
In CH ₃ NO ₂						
Nitrobenzene	1	o:m:p = 10.0:88.5:1.5				
<i>o</i> -Nitrotoluene	384	1.0	59.0	0.1	39.9	
<i>m</i> -Nitrotoluene	91	42.1		18.6	35.8	3.5
<i>p</i> -Nitrotoluene	147		99.8			0.2
In 96% H ₂ SO ₄						
Nitrobenzene	1	o:m:p = 7.1:91.5:1.4				
<i>o</i> -Nitrotoluene	545	0.6	70.5	0.1	28.8	
<i>m</i> -Nitrotoluene	138	28.4		9.9	60.1	1.6
<i>p</i> -Nitrotoluene	217		99.8			0.2

^a NT = nitrotoluene; NB = nitrobenzene. ^b The results are the average of three independent determinations and are accurate to better than ±5%.

Table II. Relative Rates and Isomer Distribution in the Nitration of *o*-Nitrotoluene and *m*-Nitrotoluene Compared to Nitrobenzene^a

ArH	Solvent	k_{NT}/k_{NB}	Isomer distribution, ^b %			o/p ^c
			Ortho	Meta	Para	
Nitrobenzene		1				
<i>o</i> -Nitrotoluene	CH ₃ NO ₂	384	39.9	1.1	59.0	0.7
	96% H ₂ SO ₄	545	28.8	0.7	70.5	0.4
<i>m</i> -Nitrotoluene	CH ₃ NO ₂	91	60.7	3.5	35.8	0.8
	96% H ₂ SO ₄	138	38.3	1.6	60.1	0.3

^a All data are from Table I. ^b For *o*-nitrotoluene, % ortho = % 2,6-dinitrotoluene, % meta = % 2,3-dinitrotoluene + % 2,5-dinitrotoluene, and % para = % 2,4-dinitrotoluene; *m*-nitrotoluene, % ortho = % 2,3-dinitrotoluene + % 2,5-dinitrotoluene, % meta = % 3,5-dinitrotoluene, and % para = % 3,4-dinitrotoluene. ^c o/p, statistically corrected; thus for *m*-nitrotoluene, o/p = 1/2 % ortho/% para.

Table I shows that the substrate selectivity changes with accompanying change in positional selectivity. The substrate selectivity is comparatively lower in nitromethane than in 96% H₂SO₄. This may be because in 96% H₂SO₄ solution the nitronium salt may interact with the water present in the system, thus decreasing the activity of the nitrating agent.

It is known that the methyl group is an ortho-para director, while the nitro group is a meta director.^{37,38} Accordingly, in *p*-nitrotoluene, the nitro group exclusively attacks the 2 position which is ortho to the methyl group and meta to the nitro group. On *o*-nitrotoluene, the nitrating agent attacks the positions meta to the nitro group and either ortho or para to the methyl group. In *m*-nitrotoluene, however, the nitrating agent attacks the 2, 4, and 6 positions, which are ortho or para to the methyl group, but not the 5 position which is meta to the nitro group. From the fact that the amount of 3,5-dinitrotoluene obtained in the nitration of *m*-nitrotoluene in both solvents is very small, it is evident that the directing effect of nitro group in comparing with that of the methyl group is negligible. In order to examine the substituent effect of the methyl group, the orienting effect of nitro group is assumed small enough to be neglected, at least as a first approximation. Thus the comparison of the relative nitration rates of nitrobenzene and *o*- and *m*-nitrotoluenes, and

the ortho/para ratio with respect to methyl group could be made, as shown in Table II.

Table II clearly shows that the nitration rates of nitrotoluenes relative to nitrobenzene are increased with decrease of the ortho/para ratio. The high substrate selectivity implies that the transition state leading to the products, according to Olah,²³ should be "late," and as postulated by Hammond,³⁹ this "late" transition state should resemble the Wheland intermediate (benzenium ion, or σ complex). The stability of the benzenium ions, consequently, should account both for substrate and positional selectivities. Thus, with higher substrate selectivity the stronger preference of an electrophile for the para position leads to a lower ortho/para ratio.

Present studies were also extended to the nitration of dinitrobenzene and dinitrotoluenes. Due to the sluggishness of *m*-dinitrobenzene toward nitrating agents, the conditions used for mononitrations were found to be unsuitable. No detectable amount of nitrated product, *i.e.*, 1,3,5-trinitrobenzene, was observed. Therefore,

more severe conditions were employed. The nitrations were carried out with nitronium tetrafluoroborate in fluorosulfuric acid solution at 95°. Under these conditions, the competitive nitration rates of 2,4-dinitrotoluene and 2,6-dinitrotoluene *vs.* *m*-dinitrobenzene could be measured. The results are shown in Table III.

Table III. Competitive Nitration of Dinitrotoluenes and *m*-Dinitrobenzene in Fluorosulfonic acid at 95°

ArH	k_{DNT}/k_{mDNB}^a	$k_{DNT}/k_{2,4-DNT}^a$
<i>m</i> -Dinitrobenzene	1	
2,4-Dinitrotoluene	468	1.0
2,6-Dinitrotoluene	2705	5.8

^a DNT = dinitrotoluene, DNB = dinitrobenzene.

Table III shows that introduction of two nitro groups in an aromatic ring has led to the relative rates of nitration of dinitrotoluenes *vs.* dinitrobenzene to be 468 for 2,4-dinitrotoluene and 2705 for 2,6-dinitrotoluene.

The nitrating agent attacks 2,4-dinitrotoluene at the position ortho to the methyl group, while it attacks 2,6-dinitrotoluene at the para position, to form 2,4,6-trinitrotoluene (TNT). It is possible to calculate the rate ratio of nitration ortho *vs.* para to the methyl group from these experiments intermolecularly. The ortho/para ratio thus obtained is 0.17, which for ni-

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tration of a toluene derivative is an extremely small value.

Noncompetitive Rate Determination. 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 method. For nitration of nitrotoluenes, a simplified flow quenching technique of Pinsent⁴⁰ was used (see Experimental Section). The rate data obtained were shown in Tables IV and V. For comparison, both relative reactivity values calculated from the separate rate determination and those from competitive reaction are also shown in these tables.

The comparison of data in Tables IV and V indi-

Table IV. 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 , $M^{-1} \text{sec}^{-1}$	$k_{2(\text{ArH})}/k_{2(\text{NB})}$
In CH_3NO_2				
Nitrobenzene	0.1-0.2	0.01-0.02	1.19×10^{-2}	1
<i>o</i> -Nitrotoluene	0.1-0.2	0.01-0.02	4.25	357 (384) ^a
<i>m</i> -Nitrotoluene	0.1-0.2	0.01-0.02	1.23	103 (91) ^a
<i>p</i> -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
<i>o</i> -Nitrotoluene	0.1-0.2	0.01-0.02	1.41	614 (545) ^a
<i>m</i> -Nitrotoluene	0.1-0.2	0.01-0.02	3.71×10^{-1}	161 (138) ^a
<i>p</i> -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 V. Rate of Nitration of *m*-Dinitrobenzene and Dinitrotoluenes in Fluorosulfonic Acid at 95°

ArH	NO_2BF_4 , M	ArH, M	k_2 , $M^{-1} \text{min}^{-1}$	$k_{2(\text{ArH})}/k_{2(\text{mNB})}$
<i>m</i> -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.

icates that the relative reactivity values obtained from the competitive method are, within the limit of the experimental error, quite consistent with those obtained from noncompetitive rate measurement.

Conclusion

Data of present study 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 1), as suggested by Schofield,⁸ in stronger acid solutions or with nitronium salts reaches limiting encounter rate. In our opinion this behavior is a direct consequence of the exothermic reaction having a very early transition state resembling starting aromatics (π complex or arenium ion nature). At the same time reported nitrations of toluene and benzene generally show high ortho/para isomer rate ratios, frequently exceeding 2. The amount of meta isomer is *always* low, ranging from 2 to 5%.

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Because it is difficult to significantly change the nature of the electrophilic nitrating agent (no weakly electrophilic, highly selective nitrating agent was reported before), 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 $k_{\text{CH}_3}/k_{\text{H}}$ 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 the 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 with increasingly predominant para orientation (in relation to the methyl group) in the nitrations 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 benzene and toluene from that of nitro(dinitro)benzene and -toluenes is 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.

From a practical point of view, our studies indicate that in the trinitration of benzene and toluene the mononitration step mechanistically is quite different from the di- and trinitration steps. This realization can be significant when considering, for example, conditions to optimize yields and to obtain highest possible regioselectivity in the preparation of TNT.

Experimental Section

Materials. Nitromethane, sulfuric acid, fluorosulfuric acid, nitrobenzene, dinitrobenzenes, 1,3,5-trinitrobenzene, nitrotoluenes, dinitrotoluenes, and 2,4,6-trinitrotoluene were all commercial materials. They were, if necessary, purified before use. Nitromethane was purified as described previously.⁴¹ Nitronium tetrafluoroborate and nitronium hexafluorophosphate were prepared according to the procedure of Olah and Kuhn,¹⁰ or the modification introduced by Kuhn.⁴²

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General Procedure for Competitive Nitration. (a) **Competitive Nitration of Nitrobenzene and Nitrotoluenes.** Nitrobenzene (0.125 mol) and nitrotoluene (0.0125 mol) were dissolved in 25 ml of nitromethane (or 96% H_2SO_4). Into this solution, 2.5 mmol of nitronium hexafluorophosphate dissolved in 25 ml of nitromethane (or 96% H_2SO_4) was added dropwise. The reaction mixture was vigorously stirred and the temperature kept constant at 25° during the reaction. The reaction time was usually 1 hr. After that, the reaction solution was quenched with water (or ice, in the case where H_2SO_4 was used as solvent), extracted with ether, washed with 5% NaHCO_3 solution, dried over MgSO_4 , concentrated, and analyzed by gas-liquid chromatography.

(b) **Competitive Nitration of *m*-Dinitrobenzene and Dinitrotoluenes.** Nitronium tetrafluoroborate (2.5 mmol) was added to 5 ml of fluorosulfuric acid in a Dry Ice-acetone bath. The resulting solution was then heated to 95°. This was then added to a solution containing 0.125 mol of *m*-dinitrobenzene and 0.0125 mol of dinitrotoluene in 25 ml of fluorosulfuric acid at 95° in an oil bath. The resulting solution was vigorously stirred and the temperature was kept constant at 95° during the reaction. The reaction time was generally 24 hr. After that, the reaction solution was quenched with ice, neutralized with sodium bicarbonate solution, extracted with ether, dried over MgSO_4 , concentrated, and analyzed by gas-liquid chromatography.

Procedure for Noncompetitive Kinetic Studies. (a) **Nitration of Nitrobenzene, *m*-Dinitrobenzene, and Dinitrotoluenes.** An appropriate concentration of nitronium salt solution was placed into a round-bottomed flask equipped with a magnetic stirring bar and kept in a constant-temperature bath. In the case, when fluorosulfuric acid was used as solvent, the nitrating solution was prepared at Dry Ice-acetone bath, and warmed up to 95°. The nitro compound solution of the same temperature was then added at once with vigorous stirring. The solution always contains excess (ten-folds) of the nitrating agent, thus ensuring first-order kinetics. Portions of the sample were withdrawn at various times and quenched with ice-water, and, after work-up, analyzed by gas chromatography. From the amount of the product and unreacted substrate, good linear pseudo-first-order plots were obtained. From these plots k_2 was calculated from the concentration of nitronium salt.

(b) **Nitration of Nitrotoluenes.** The rates of nitration of nitrotoluenes are so fast that it is difficult to withdraw samples by conventional method during reaction. Therefore, a simplified flow-quenching apparatus of Pinsent⁴⁰ was designed as shown in Figure 1.

In Figure 1, A and B are 50-ml syringes driven by a syringe pump C (Sage Instruments, Model 351), D and E are two flexible 1/8-in. Teflon tubings (0.055 in. i.d.), F, a Swagelok union tee with inside diameter of 0.042-in., is used as a simplified mixing chamber, and G is one of seven 1/8-in. stainless steel tubings (0.055-in. i.d.) with various lengths (from 5 to 60 cm). D, E, F, and most part of G except the opening end are immersed in a constant-temperature bath.

Solutions of substrate and nitrating agent are placed in A and B, respectively. As the syringe pump, C, moves, the solutions in A and B are forced to mix at F and then pass along G, where the reaction occurs, and was quenched at the end of G. The reaction time is determined by the flow rate of the solution and the length of G. In each set of experiments, seven quenching products were obtained by using tubings G of various length, while the flow rate was kept constant. The time of quenching was then calculated and the quenching products were worked up and analyzed by gas chromatography. From the amount of products and the unreacted substrate, good linear pseudo-first-order plots were obtained. From these plots k_2 was calculated from the concentration of the nitronium salt.

The reproducibility of the results obtained from the present flow-quenching technique is illustrated in Table VI, showing the kinetic data of three parallel sets of experiments of nitration of *o*-nitrotoluene with nitronium hexafluorophosphate in nitromethane solution at 25°.

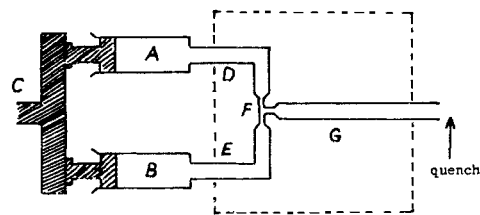


Figure 1. Simplified flow-quenching apparatus for nitration of nitrotoluene (not to scale).

Table VI. Illustration of Reproducibility of Nitration of *o*-Nitrotoluene with Nitronium Hexafluorophosphate in Nitromethane Solution at 25° by Flow-Quenching Technique

Experiment	Flow rate, ml/sec	k_2 , $M^{-1} \text{sec}^{-1}$
a	1.9	4.16
b	2.3	4.24
c	2.1	4.35

Analytical Procedure. The analyses of all products were carried out by gas-liquid chromatography, using a Perkin-Elmer Model 900 gas chromatograph equipped with a hydrogen flame ionization detector and either open tubular capillary columns (for competitive reactions) or packed columns (for noncompetitive kinetic studies). Peak areas were obtained with an Infotronics Model CRS-100 electronic printing integrator. Relative response data were determined as reported previously.

Characteristic retention times of the nitro compounds along with type of Golay capillary columns employed and column condition are listed in Table VII.

Table VII. Gas-Liquid Chromatographic Analysis Data

Nitro compound	Column ^a	Conditions ^b of column	Retention time, sec
Nitrobenzene	A	III	597
<i>o</i> -Nitrotoluene	A	III	684
<i>m</i> -Nitrotoluene	A	III	805
<i>p</i> -Nitrotoluene	A	III	897
<i>o</i> -Dinitrobenzene	B	I	338
<i>m</i> -Dinitrobenzene	B	I	252
<i>p</i> -Dinitrobenzene	B	I	233
2,3-Dinitrotoluene	B	I	312
2,4-Dinitrotoluene	B	I	305
2,5-Dinitrotoluene	B	I	249
2,6-Dinitrotoluene	B	I	204
3,4-Dinitrotoluene	B	I	491
3,5-Dinitrotoluene	B	I	328
1,3,5-Trinitrobenzene	B	II	2435
2,4,6-Trinitrotoluene	B	II	1911

^a A, a stainless steel open tubular column, 150 ft \times 0.01 in. wall coated with butanediol succinate; B, a stainless steel open tubular column, 100 ft \times 0.02 in. wall coated with butanediol succinate. ^b Column conditions (column temperature, °/carrier gas, helium, pressure, psi): I, 180/30; II, 170/30; III, 160/20.

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