[3] *F. Percheron*, Ann. Chim. *7* [13], 342 (1959).
[4] *U. Renner, K. A. Jaeggi & D. A. Prins*, Tetrahedron Letters *1965*, 3697.
[5] *G. Büchi & E. W. Warnhoff*, J. Amer. chem. Soc. *81*, 4433 (1959).
[6] *M. Hesse*, Fortschritte der Massenspektrometrie, Vol. 1 «Indolalkaloide», Verlag Chemie, Weinheim 1974.
[7] ^{13}C-NMR von Indol-Alkaloiden (excl. Oxindol-Derivate): *E. Wenkert, J. S. Binda, C.-J. Chang, D. W. Cochran & F. M. Schell*, Accounts chem. Res. *7*, 46 (1974) (Übersichtsartikel); *E. Wenkert, D. W. Cochran, E. W. Hagaman, F. M. Schell, N. Neuss, A. S. Katner, P. Potier, C. Kan, M. Plat, M. Koch, H. Mehri, J. Poisson, N. Kunesch & Y. Rolland*, J. Amer. chem. Soc. *95*, 4990 (1973) (*Aspidosperma*-Alkaloide); *R. H. Levin, J.-Y. Lallemand & J. D. Roberts*, J. org. Chemistry *38*, 1983 (1973) (*Rauwolfia*-Alkaloide); *N. Neuss, H. E. Boaz, J. L. Occolowitz, E. Wenkert, F. M. Schell, P. Potier, C. Kan, M. M. Plat & M. Plat*, Helv. *56*, 2660 (1973); *P. Yates, F. N. MacLachlen, I. D. Rae, M. Rosenberger, A. G. Szabo, C. R. Willis, M. P. Cava, M. Beforous, M. V. Lakshmikantham & W. Zeiger*, J. Amer. chem. Soc. *95*, 7842 (1973); *M. P. Cava, M. V. Lakshmikantham, S. K. Talapatra, P. Yates, I. D. Rae, M. Rosenberger, A. G. Szabo, B. Douglas & J. A. Weisbach*, Canad. J. Chemistry *51*, 3102 (1973); *C. Kan, G. Massiot, A. Ahond, B. C. Das, H.-P. Husson, P. Potier, A. I. Scott & C.-C. Wei*, J. chem. Soc. (Chem. Commun.) *1974*, 164; *A. Cavé, J. Bruneton, A. Ahond, A.-M. Bui, H.-P. Husson, C. Kan, G. Lukas & P. Potier*, Tetrahedron Letters *1973*, 5081; *R. E. Moore & H. Rapoport*, J. org. Chemistry *38*, 251 (1973); *F. W. Wehrli*, J. chem. Soc. (Chem. Commun.) *1973*, 379; *A. Ahond, M.-M. Janot, N. Langlois, G. Lucacs, P. Potier, P. Rasoanaivo, M. Sangaré, N. Neuss, M. Plat, J. Le Men, E. W. Hagaman & E. Wenkert*, J. Amer. chem. Soc. *96*, 633 (1974) (Vindolinin).
[8] *S. Savaşkan, I. Kompiš, M. Hesse & H. Schmid*, Helv. *55*, 2861 (1972); *H. O. Bernhard, I. Kompiš, S. Johne, D. Gröger, M. Hesse & H. Schmid*, ibid. *56*, 1266 (1973).
[9] *R. Hollenstein & W. v. Philipsborn*, Helv. *55*, 2030 (1972).

---

30. The Nitration of Pentamethylbenzene with Nitronium Hexafluorophosphate and Water in Nitromethane

by **Erich Hunziker, Philip C. Myhre**¹), **John R. Penton**
and **Heinrich Zollinger**

Department of Industrial and Engineering Chemistry, ETH, 8006 Zürich

(5. XI. 74)

Summary. The nitration of pentamethylbenzene in nitromethane has been studied under conditions that allow two mechanisms of nitration to be distinguished. One has been identified as nitration *via* the nitronium ion; the other nitration involves an oxidation of the molecular complex $\mathrm{ArH{-}NO^{\oplus}PF_6^{\ominus}}$ by nitrogen dioxide followed by reaction of the aromatic substrate with the incipient nitronium ion and loss of nitric oxide. Either reaction can be made predominant by an appropriate change in the proportions of the reactants in the system.

A consideration of the σ-complexes formed by attack of the electrophile at aromatic carbon bearing a methyl substituent can provide a satisfactory explanation for the features observed in this and in other nitrations of pentamethylbenzene.

1. Introduction. – The process of electrophilic substitution in polymethylated benzenes and their derivatives has received considerable attention [1–7]. Fully substituted compounds such as hexamethylbenzene undergo substitution in a side-chain methyl group [4] [5] [6b]. It has been suggested that these reactions proceed *via* the

---

¹) Guest Professor ETH 1971–72. Permanent address: Department of Chemistry, Harvey Mudd College, Claremont, California 91711.

formation of cyclohexadiene intermediates followed by a migration of the substituent group from the nucleus to the side-chain [4] [5]. Similar reactions occur in the corresponding nitrations of compounds which possess unsubstituted positions, *e.g.* durene and pentamethylbenzene, but the nature and proportions of the products formed depend on the reaction conditions. Thus, the nitration of durene with mixed acid (HNO_3/H_2SO_4) in acetonitrile gives 90% by-product, but when the solvent is changed to nitromethane mononitrodurene is the main product [2].

Nitration of pentamethylbenzene with fuming nitric acid in chloroform or nitromethane produces some pentamethylnitrobenzene together with by-products (60–90%); the nature of the by-products can be accounted for if 2,3,4,5-tetramethylbenzyl nitrate is formed initially in the reaction [6c] [7]. A mechanism suggested involved attack of the nitronium ion at the position bearing hydrogen, followed by proton loss from an α-methyl group. An intramolecular rearrangement of the nitro group then leads to the formation of a nitrite ion which would be oxidized rapidly by nitric acid to the corresponding nitrate [7]. The role played by steric effects was emphasized, and it was considered that proton loss from a methyl group can compete effectively with proton loss from the nucleus in the 'crowded' pentamethylbenzene molecule.

Evidence for the nitronium ion as the effective electrophile, and for the existence of a common intermediate along the reaction path was adduced from the effects of added species (NO_3^-, H_2SO_4, NO_2^-) on the rate of reaction and on the nature of the products formed [7]. The addition of nitrate ion (4.4%)[2] anticatalyzed the reaction without altering the side-chain nitrooxylation/nuclear nitration ratio to a large extent; and sulfuric acid (2%)[2] catalyzed the reaction, producing at the same time, however, an increase of almost 100% (14 → 24%) in the amount of pentamethylnitrobenzene formed.

The effects of these added species on the rate of reaction are consistent with nitration *via* the nitronium ion, but the magnitudes of these effects were far smaller than those normally observed in nitrations with nitric acid in nitromethane [8]. Furthermore, the observation that durene and pentamethylbenzene underwent a much faster reaction than mesitylene is in direct conflict with earlier work [8] in which the nitrations of benzene and its homologs with nitric acid in nitromethane were shown to be zeroth-order with respect to the aromatic compound. Finally, the enhancement in rate brought about by the addition of nitrite ion (0.9%)[2] strongly suggests that oxides of nitrogen are involved in these reactions.

Under conditions where the effective electrophile is the nitronium ion, *i.e.* in nitrations with nitronium salts in aprotic solvents, the nature and proportions of the products formed in the nitrations of durene and pentamethylbenzene depend on the process of mixing. Little, if any by-products arise from attack by the nitronium ion on the parent compound [2] [3]. By-products are formed in the nitration of pentamethylbenzene with nitronium hexafluorophosphate in acetonitrile; their nature is, however, consistent with an attack by the nitronium ion on pentamethylnitrobenzene which is formed initially [3]. These results suggest that under certain conditions of nitration both durene and pentamethylbenzene are capable of undergoing a 'normal' nitration with the nitronium ion, and that proton loss from a methyl group does not occur, to any large extent, in the dinitration of the former compound and in the mononitration of the latter compound.

To investigate the factors that influence the course of the nitration of pentamethylbenzene, we have studied the nitration of this hydrocarbon in nitromethane with the nitrating system, nitronium hexafluorophosphate and water. This work represents an extension of earlier studies of the nitration of durene with the same nitrating system [2]. Those studies indicated autocatalysis, and it is that feature that represents a focus of much of the experimental work reported here.

[2] With respect to the concentration of fuming nitric acid (0.5 M).

2. Results. – 2.1. *General Characteristics Exhibited by the Reaction.* The standard reaction in this study consisted of a mixture of pentamethylbenzene (0.025 M), nitronium hexafluorophosphate (0.025 M) and water (0.05 M) in nitromethane at 20°[3]). Reactions were initiated by rapid mixing of equal volumes of a nitromethane solution of pentamethylbenzene and a nitromethane solution containing both the nitronium salt and water to give a reaction solution of the desired concentration and stoichiometry. It should be noted that the nitronium salt used in this study contained about 12% nitrosonium hexafluorophosphate. The actual composition of the nitromethane stock solution containing the nitronium plus nitrosonium salt and water will be a subject of discussion in later sections[4]).

Preliminary studies showed that the formation of pentamethylnitrobenzene with time followed an S-shaped curve analogous to that observed in the nitration of durene under similar conditions (see Fig. 2 in [2]). However, repetitive runs showed that composition *vs.* time profiles, obtained by removing aliquots from a stoppered reaction vessel, were not reproducible. The time of onset of autocatalysis varied; in some cases no induction period was observed. The cause of these variations was traced to adventitious water, above the amount added deliberately. Subsequent studies were carried out with the use of V-tubes which were charged in a dry box. Details of the method are described in the experimental part.

The use of these more rigorous conditions improved the reproducibility of the reaction *vs.* time profiles. Nevertheless, the sensitivity of the reaction to adventitious water made it necessary to conduct a parallel standard reaction when testing the effects of added species or variations in reactant concentrations.

Under these carefully controlled reaction conditions, the standard reaction profile (Fig. 1) exhibited two distinct stages.

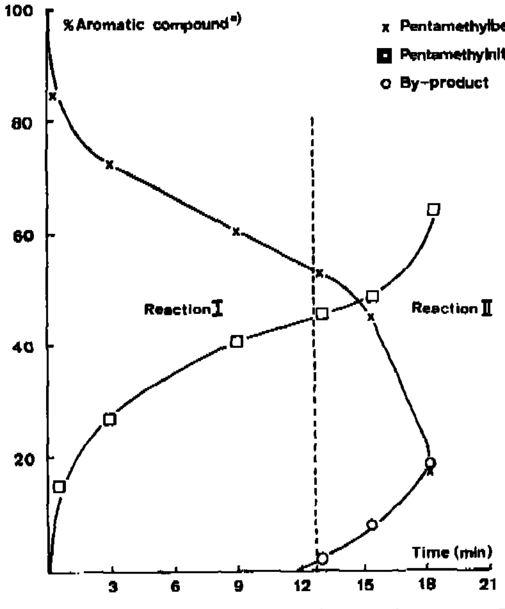


Fig. 1. *The Nitration of Pentamethylbenzene* (0.025 M) *with Nitronium Hexafluorophosphate* (0.025 M) (*containing 11.8% Nitrosonium Hexafluorophosphate*) *and Water* (0.05 M) *in Nitromethane at 20°*
a) Determined by gas chromatography.

---

[3]) Concentrations shown in the text are after mixing.

[4]) The nitronium salt concentrations given in this account include impurity nitrosonium salt.

During the first stage, pentamethylnitrobenzene is formed with no more than a trace amount of by-product. In the second stage, pentamethylnitrobenzene and by-products are formed in approximately equal amounts. It will be convenient to discuss separately the experimental studies designed to characterize the underlying reactions in these two stages of reaction.

2.2. Experimental Studies of Stage I. Information concerning the first stage of the reaction profile was obtained by a study of the effects of added species and variations in reactant concentration.

The marked effect of water on the reaction profiles is shown in Fig. 2.

In this study the profile of a standard reaction was compared with the profiles of three related reactions differing only in the number of equivalents of water added. When slightly less than two equivalents of water was added, the initial rate of formation of pentamethylnitrobenzene was accelerated. A deceleration of the initial rate of nitration was observed with slightly more than two equivalents of water. However, when the water concentration was increased to about three equivalents, the onset of stage II was immediate, as judged by the rapid increase in both pentamethylnitrobenzene and by-products.

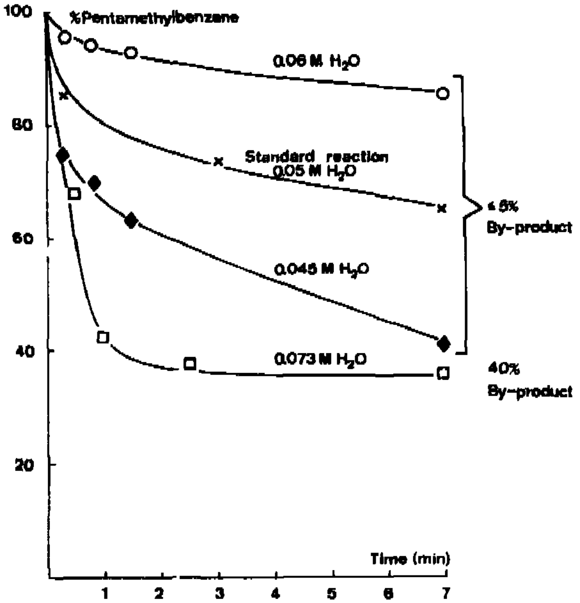


Fig. 2. *The Effect of Water on the Characteristics shown by the Standard System*

Variations in the concentration of the aromatic reactant or changes in the nature of the aromatic reactant produced essentially no change in the initial rate of nitration. Thus, when the reference reaction was varied by increasing the pentamethylbenzene concentration by a factor of five the initial rate of nitration remained essentially unchanged (see Fig. 3). Furthermore, both mesitylene and benzene underwent nitration under the standard reaction conditions at the same initial rate. It must be concluded that nitration during stage I of the reaction is zeroth-order with respect to the aromatic reactant.

It was also observed that addition of dinitrogen tetroxide (0.006 M)5) to the system reduced the initial rate of reaction by a factor of about two and brought forward the onset of stage II of the reaction profile.

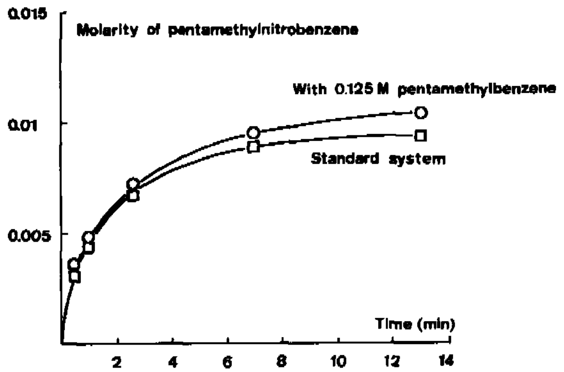


Fig. 3. *The Effect of an Increase in the Concentration of Pentamethylbenzene on the Characteristics shown by the Standard System*

The most surprising result was the observation that sulfuric acid was catalytically ineffective. Addition of 99.2% sulfuric acid (0.025 M) to the standard reaction had no effect on the initial rate of nitration. By contrast, addition of 96% sulfuric acid depressed the initial rate and altered the character of the reaction profile (see Fig. 4 & 5).

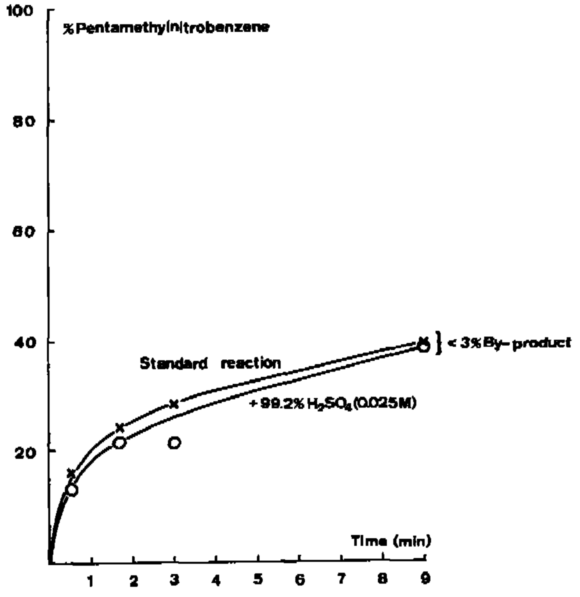


Fig. 4. *The Effect of the Addition of 99.2% H_2SO_4* (0.025 M) *to the Standard Reaction*

---

5) The concentrations of the reactants used in this reaction and in the reaction used for comparison purposes were double those of the standard reaction.

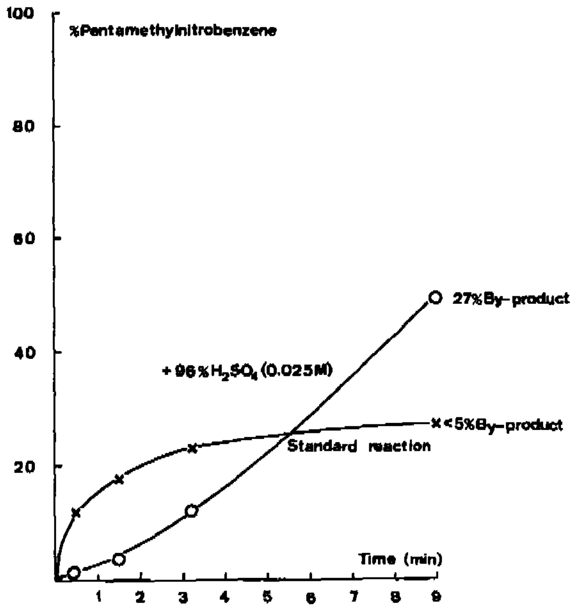


Fig. 5. *The Effect of the Addition of 96% H_2SO_4* (0.025 M) *to the Standard Reaction*

2.3. *Experimental Studies of Stage II.* Studies of the change in nitrous acid concentration during the course of reaction indicated that the onset of Stage II could be correlated with an increase in the concentration of lower oxides of nitrogen. As shown by representative data in Table 1, Stage I of the reaction proceeds with only a small increase in nitrous acid concentration (11.8 → 13.4%), but after onset of Stage II the nitrous acid concentration increased sharply (13.4 → 18.2%).

Table 1. *The concentration of nitrous acid at various times during the standard reaction*[a])

Time [s]	% Pentamethylbenzene	% Pentamethylnitrobenzene	% Nitrous acid[b])
40	84.5	14.7	12.1
60	83.3	19.4	
135	69.7	27.4	
265	70.3	31.0	12.5
725	53.6	45.2	12.6
1087	47.5	50.8	13.4
1510	21.6	69.4	18.2

[a]) See Fig. 1 for the concentrations and conditions employed.

[b]) 11.8% before reaction. Estimated error: ± 1% of the value shown.

Not all aromatic hydrocarbons exhibit the autocatalytic stage II. For example, when mesitylene was nitrated under conditions identical to those listed in Table 1, 47% of the reactant was converted to nitromesitylene after 1500 s and the nitrous acid concentration had increased only slightly (11.8 → 13.8%).

Earlier observations showed that pentamethylbenzene reacts reversibly with nitrosonium ion in anhydrous nitromethane to form a π-complex, but reaction does not proceed to substitution product [3]. Additional experiments demonstrated that no reaction products are formed even when a threefold excess of nitrosonium salt is used. However, a reaction does occur between pentamethylbenzene, nitrosonium hexafluorophosphate and water in nitromethane solution. Results of studies are shown in Table 2 (rows 1 and 2).

After 170 s, pentamethylnitrobenzene (5.3%) and by-products (23.1%) are formed, one of the latter having the same retention time on the gas-chromatograph as an authentic sample of 2,3,4,5-tetramethylbenzaldehyde, a compound which is formed in stage II. The reaction slows down after this time and only 12% of the pentamethylbenzene remaining undergoes reaction in the next 27 min.

An increase in the rate of reaction and a marked change in product distribution was observed (Table 2, rows 3 and 4) when the reaction conditions were altered by allowing a preformed nitromethane solution of the pentamethylbenzene-nitrosonium hexafluorophosphate complex to react with a nitromethane solution of the nitrosonium salt and water.

Table 2. *The reaction between pentamethylbenzene, nitrosonium hexafluorophosphate and water in nitromethane at 20°* [a])

Reactants	Time [s]	% Pentamethylbenzene	% Pentamethylnitrobenzene	% Aldehyde [b])	% Unidentified By-Products
ArH (0.05 M)	170	71.6	5.3	8.0	15.1
$NO^{\oplus}PF_6^{\ominus}$ (0.05 M)					
H_2O (0.10 M)	1800	62.8	7.0	9.3	20.9
ArH (0.05 M)	170	63.8	20.4	–	15.8
$NO^{\oplus}PF_6^{\ominus}$ (0.1 M)					
H_2O (0.1 M)	1800	49.1	30.8	–	20.1

a) For details of the method, see experimental part.

b) 2,3,4,5-Tetramethylbenzaldehyde.

Table 3. *The reactions of pentamethylbenzene, and of the complex ArH—$NO^{\oplus}PF_6^{\ominus}$ with dinitrogen tetroxide in nitromethane at 20°*

	Time [s]	% Pentamethylnitrobenzene	% By-Products
	120	0.8	18.2
ArH (0.05 M)	360	2.1	29.5
N_2O_4 (0.05 M)	900	3.7	45.4
	1800	4.9	63.1
	11	17.1	11.5
	30	25.7	20.4
ArH (0.042 M)	50	35.0	15.2
$NO^{\oplus}PF_6^{\ominus}$ (0.042 M)	90	44.2	15.3
N_2O_4 (0.042 M)	122	47.4	18.0
	207	57.2	16.0
	360	72.0	19.1

These results indicated possible dinitrogen tetroxide catalysis of aromatic nitration by the nitrosonium ion (see discussion), and to explore this question in more detail the reaction of nitromethane solutions of pentamethylbenzene and dinitrogen tetroxide in the presence and absence of added nitrosonium salt were studied. It is immediately apparent from the data (Table 3)[6]) that reaction occurs at a much faster rate when nitrosonium hexafluorophosphate is present in the reaction solution. In addition, the reaction solution containing nitrosonium salt yields a much higher ratio of nitration product to by-products. Thus dinitrogen tetroxide reacts with pentamethylbenzene at a moderate rate to yield mainly by-products which include tetramethylbenzaldehyde and tetramethylbenzyl alcohol. Addition of a stoichiometric equivalent of nitrosonium hexafluorophosphate to the reaction mixture results in a greatly increased reaction rate, apparently by accelerating the rate of formation of pentamethylnitrobenzene.

Another set of studies involving the reaction of dinitrogen tetroxide and pentamethylbenzene together with varying amounts of nitrosonium salt or nitric acid were carried out to investigate whether by-product formation and nitration were independent or connected paths. The results (Table 4) indicated small but increased rates and yields of nitration product when the reaction conditions favored an increased concentration of the molecular complex formed from the aromatic and nitrosonium ion.

Table 4. *The effect of increasing the concentration of the complex in the reaction between the complex and dinitrogen tetroxide in nitromethane at 20°*

Reactants	Time [s]	% Pentamethylnitrobenzene	% By-product
	120	44.5	13.3
ArH (0.025 M)	300	57.7	19.0
$NO^{\oplus}PF_6^{\ominus}$ (0.025 M)	600	68.1	22.0
N_2O_4 (0.025 M)	1800	72.9	24.4
ArH (0.025 M) $NO^{\oplus}PF_6^{\ominus}$ (0.025 M) N_2O_4 (0.025 M) HNO_3 (0.025 M)	120	13	23.3
ArH (0.025 M)	120	48.5	9.3
$NO^{\oplus}PF_6^{\ominus}$ (0.050 M)	300	65.7	13.7
N_2O_4 (0.025 M)	600	75.6	17.0
	1800	81.0	17.9

The rates of nitration of pentamethylbenzene and mesitylene by nitrosonium hexafluorophosphate/dinitrogen tetroxide 1:1 were investigated. The profiles for these reactions (Fig. 6) clearly demonstrate that under these reaction conditions the rate of formation of pentamethylnitrobenzene is much faster than the rate of formation of nitromesitylene. The increase in the concentration of pentamethylnitrobenzene with time was paralleled by a decrease in the concentration of the molecular complex.

---

[6]) In the reaction of the complex with dinitrogen tetroxide yields of up to 86% pentamethylnitrobenzene were obtained in some experiments with solvent distilled three times from P_2O_5.

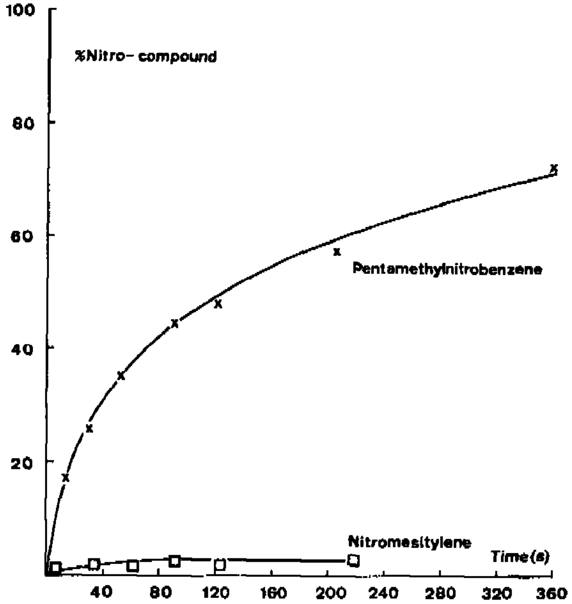


Fig. 6. *The Reactions of Dinitrogen Tetroxide with the Molecular Complexes formed between Pentamethylbenzene, Mesitylene, and Nitrosonium Hexafluorophosphate in Nitromethane at 20°.* Reactant Proportions: $ArH/NO^{\oplus}PF_6^{\ominus}/N_2O_4$ = 0.042 M: 0.042 m: 0.042 M.

Further information concerning the mechanism of this reaction was obtained from kinetic studies. At a constant dinitrogen tetroxide concentration, the initial rate of formation of pentamethylnitrobenzene was doubled when the concentration of the complex was increased twofold; the reaction is thus first-order with respect to the complex. A determination of the order with respect to dinitrogen tetroxide requires a knowledge of its dissociation constant in nitromethane. This has not been measured, but in acetonitrile $K_{25} = 0.3 \pm 0.1 \times 10^{-4}$ mol l^{-1} [9]. All subsequent kinetic studies were therefore carried out in this solvent.

At 20° and a dinitrogen tetroxide concentration of 0.025 M the reaction was too fast for convenient study, but a product distribution similar to that observed in nitromethane was found (see Table 3). Further experiments showed that the kinetics of the reaction could be studied at 5°, and at this temperature the product distribution was essentially unchanged from that found at 20°.

Table 5. *Rates of reaction of the pentamethylbenzene-nitrosonium salt complex* [0.0025 M] *with different stoichiometric concentrations of dinitrogen tetroxide in acetonitrile at 5°*

10^2 $[N_2O_4]_{st}$	10^4 $[NO_2]_{eq}$	10^4 k_1 $[s^{-1}]$	10^2 $k_1/[N_2O_4]_{eq}$ $[l\ mol^{-1}\ s^{-1})]$	$k_1/[NO_2]_{eq}$ $[l\ mol^{-1}\ s^{-1}]$
7.13	5.53	8.68	1.22	1.57
4.75	4.52	7.99	1.69	1.77
2.38	3.19	4.56	1.93	1.43
1.43	2.47	4.13	2.90	1.67
0.95	2.01	3.67	3.90	1.82

The results of a series of experiments with a constant concentration of complex and various concentrations of dinitrogen tetroxide are shown in Table 5.

The reactions were followed by recording the decrease in the complex concentration spectrophotometrically at 500 nm. Under the conditions shown in the table, pseudo first-order kinetics were observed. A typical example is shown in Fig. 7; a plot of log (OD_∞ – OD_t) against time is linear for over 90% reaction. The pseudo first-order rate constants were calculated from the slopes of such plots. Division of these rate constants by the equilibrium concentration of dinitrogen tetroxide or nitrogen dioxide allows a distinction to be made between the rate equations: rate = k_2[complex]$[N_2O_4]^x$ and rate = k_2[complex]$[NO_2]^y$.

The value of the dissociation constant of dinitrogen tetroxide in acetonitrile at 5°, $K_5 = 0.043 \pm 0.014 \times 10^{-4}$ mol l^{-1}, was calculated from the *van't Hoff* equation using the previously determined value of K_{25} and $\Delta H = 16$ kcal mol^{-1} [9]. The concentration of nitrogen dioxide at equilibrium was obtained from $[NO_2] = \{K^2/16 + K[N_2O_4]_{st}\}^{1/2} - K/4$. The last two columns of Table 5 show quite clearly that the reaction is represented by the rate equation, rate = k_2[complex]$[NO_2]$.

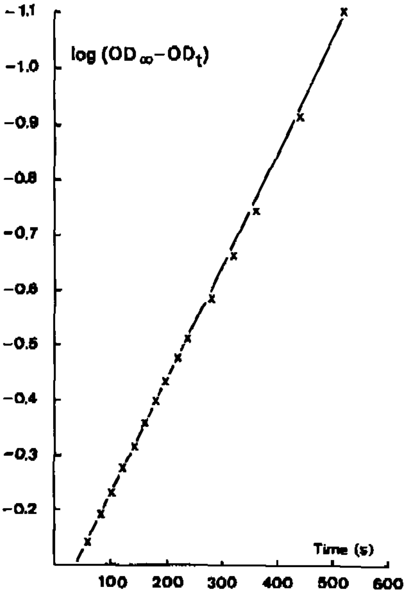


Fig. 7. *First-Order Plot for the Reaction of the Complex* (0.0025 M) *with Dinitrogen Tetroxide* (0.071 M) *in Acetonitrile at* 5°

Finally, the kinetic isotope effect in the reaction was investigated by the competitive method. The reaction of dinitrogen tetroxide (0.005 M) with the complexes formed between nitrosonium hexafluorophosphate (*0.1 M*), *pentamethylbenzene* (*0.05 M*) *and pentamethylbenzene-1-d_1* (*0.05 M*) in nitromethane at 20° gave 85% pentamethylnitrobenzene and 15% by-product on completion. Examination of the unreacted aromatics by mass spectroscopy showed $k_H/k_D = 1 \pm 0.2$.

2.4. *The Products formed in Stage II.* An attempt was made to determine the nature and proportions of the by-products formed under the conditions of the standard reaction. 2,3,4,5-Tetramethylbenzyl nitrate, a product found in fuming nitric acid nitration of pentamethylbenzene [7], was not found in the IR. spectrum of the products. Test mixtures subjected to the work up procedure showed that this compound could be identified by its O–N–O infrared stretching frequency (1635 cm^{-1}) in concentrations of *ca.* 5% in the standard reaction.

Gas-chromatography of the product mixture showed the presence of pentamethylnitrobenzene (61%) and a compound with the same retention time as 2,3,4,5-tetramethylbenzaldehyde (1.5%). By contrast, thin layer chromatography showed that at least ten by-products were present. Of these it was found possible to isolate and identify unambiguously only one: 2,2′,3,3′,4,4′,5,5′,6-nonamethyldiphenylmethane (1.7%). The compound previously identified as 2,3,4,5-tetramethylbenzaldehyde by gas-chromatography was isolated and its IR. spectrum was identical with that of an authentic sample. One other product was isolated whose IR. spectrum resembled that of 6-nitro-2,3,4,5-tetramethylbenzyl nitrate, but too little material was obtained to enable a positive identification to be made.

Attempts were made to obtain compounds which resembled the unidentified by-products formed in stage II from other nitration systems. However, the nitrations of pentamethylbenzene with fuming nitric acid and with mixed acid (HNO_3/H_2SO_4) in nitromethane produced so many by-products that their isolation was impracticable.

One by-product which was formed in the standard reaction decomposed on quenching the solution. It had a deep red-purple color and its rate of formation in most cases (but not all) increased rapidly during stage II. This was seen by an examination of the VIS. spectrum of the reaction. The optical density expected for the molecular complex formed between the aromatic reactant and nitrosonium ion in the standard reaction is 0.25 (650 nm, 1 cm cell) if no water were present. However, in this reaction the initial optical density was 0.33 (650 nm, 1 cm cell) rising to 0.4 at the end of stage I, and then further increasing to 0.7 on completion of stage II. It is possible that the formation of a diaryloxidoammonium ion [10] can account for this increase in optical density. If this is the case use of data [10] for the extinction coefficient of dianisyloxidoammonium perchlorate enables an estimate to be made of the concentration of the colored by-product formed in the standard reaction. This turns out to be $<0.5\%$ at the end of stage I, increasing to *ca.* 1% on completion of stage II.

2.5. *Related Nitration Systems.* For comparison, the nitrations of pentamethylbenzene in related nitration systems were studied. Nitrations were carried out with fuming nitric acid in nitromethane and acetonitrile with and without the addition of sulfuric acid. The results are shown in Table 6.

In nitromethane, nitration with fuming nitric acid gives a large number of by-products, some of which had similar retention times on the gas-chromatograph to the by-products formed in the reaction between pentamethylbenzene and dinitrogen tetroxide; their nature was, however, not investigated further. Addition of sulfuric acid results in an increase in the rate of nitration and an increase in the proportion of pentamethylnitrobenzene formed.

The situation in acetonitrile is somewhat different. Here sulfuric acid catalyses the reaction, but even with two equivalents of acid, a relatively low yield of pentamethylnitrobenzene is found. The IR. spectrum of the products of this reaction had principal bands at 3400 cm^{-1}, 2920 cm^{-1} and 1660 cm^{-1} closely resembling the spectrum of N-acetyl-2,3,4,5-tetramethylbenzylamine, a compound which could be formed by attack of the solvent on the aromatic [3].

The unusual features of these nitrations in acetonitrile prompted a more detailed investigation. The results of kinetic and partition isotope studies are shown in Table 7. Competitive nitration of pentamethylbenzene and pentamethylbenzene-1-d, showed that no kinetic isotope effect occurred in the reaction.

In the studies of the partition isotope effect, a mixture of pentamethylbenzene-1-d, and pentamethylbenzene-1-α-d_3 was reacted with a mixture of nitric and sulfuric acid; and the nitro-compounds were examined by gas-chromatography and mass-spectroscopy. The partition isotope effect was calculated from the relation:

$$\left(\frac{[\text{nitro}]}{[\text{by-prod}]}\right)_{\mathrm{H}} \cdot \left(\frac{[\text{by-prod}]}{[\text{nitro}]}\right)_{\mathrm{D}} = \frac{(5\,k_{\mathrm{H}} + k_{\mathrm{D}})}{6\,k_{\mathrm{H}}}$$

The significance of these results is discussed later.

Table 6. *The effect of the addition of sulfuric acid* (98%) *on the nitration of pentamethylbenzene with fuming nitric acid in nitromethane and acetonitrile at 20°*

Reactant concentrat. [mol l^{-1}]			Conditions	Products		
Pentamethylbenzene	HNO_3	H_2SO_4		% Pentamethylbenzene	% Pentamethylnitrobenzene	% By-product
0.1	0.1	–	CH_3NO_2	40.0	7.6	52.4
0.1	0.1	0.1	3 h	28.6	42.8	28.6
0.1	0.1	0.2		8.3	68.8	22.9
0.1	0.1	–	CH_3CN	87.4	0.5	12.1
0.1	0.1	0.1	3 h	27.5	4.8	67.7
0.1	0.1	0.2		17.2	13.5	69.3

Table 7. *Kinetic and partition isotope effects in the nitration of pentamethylbenzene with mixed acid in acetonitrile at 20°*[a])

Reactants [mol l^{-1}]			Products			
Aromatic	HNO_3	H_2SO_4	% Pentamethylnitrobenzene	% By-product	k_H/k_D	(k_D/k_H) nitro by-product
0.2	0.02	0.04	15.0[b])	85.0[b])	1.0 ± 0.2	–
0.09	0.11	0.22	9.1	90.9	–	3.8 ± 1.2[c])

[a]) Full details are given in the experimental part.

[b]) With respect to the concentration of fuming nitric acid.

[c]) For proton loss from the α-methyl groups.

3. Discussion of the Experimental Results. – The reaction of pentamethylbenzene with nitronium plus nitrosonium salts and water is complex. However, a number of features have been established by kinetic study, and these results permit mechanistic discussion. Part of the reaction complexity arises from the fact that the system under study is closely related to a preparative reaction; it differs significantly from systems normally used to study mechanistic features of aromatic nitration. For example, nearly all of the reactant species undergo large concentration changes as the reaction progresses. However, the reaction system does allow a fairly clear separation of at least two distinct paths of nitration. Additionally, it is possible that the results obtained in studies of this type may be more easily connected to the general behavior observed when certain polyalkylbenzenes are subjected to preparative nitration reactions.

In the discussion to follow we shall first consider the state of the system at the start of reaction. Next, a mechanistic discussion of the regions identified as stage I and stage II of the reaction profile will be presented, and areas of mechanistic uncertainty will be identified. Finally, we shall consider these results together with data collected for related nitration systems.

3.1. *Equilibria in the Reaction System.* First, some discussion concerning the kind and concentration of species present in the reaction system must be made. The possible species can be organized into four groups of equilibria that can obtain at the start of reaction.

The first group of equilibria represent possible species formed by reaction of water with nitronium hexafluorophosphate.

$$NO_2^{\oplus}PF_6^{\ominus} + H_2O \rightleftarrows H_2NO_3^{\oplus}PF_6^{\ominus} \rightleftarrows HNO_3 + H^{\oplus}PF_6^{\ominus} \qquad (1a)$$

$$H_2NO_3^{\oplus}PF_6^{\ominus} + H_2O \rightleftarrows HNO_3 + H_3O^{\oplus}PF_6^{\ominus} \qquad (1b)$$

It is assumed that equations 1a and 1b lie far to the right when one equivalent of nitronium salt and two equivalents of water are mixed in nitromethane. The existence of significant concentrations of $H^{\oplus}PF_6^{\ominus}$ is considered improbable [11]. Thus we shall treat the standard system at the start of the reaction as if it contained nearly one equivalent of nitric acid and one equivalent of the ion pair, hydronium hexafluorophosphate.

The fact that the nitronium salt used in this study contained about 10–12% nitrosonium hexafluorophosphate complicates the situation considerably. We must also consider the analogous equilibria (eq. 2a and 2b) involving nitrosonium ion and water. These equilibria do not lie as far to the right as do the equilibria shown in equations 1a and 1b. This is consistent with the relative pK_R values of nitric and nitrous acids in strong aqueous acid media.

$$NO^{\oplus}PF_6^{\oplus} + H_2O \rightleftarrows H_2NO_2^{\oplus}PF_6^{\ominus} \rightleftarrows HNO_2 + H^{\oplus}PF_6^{\ominus} \qquad (2a)$$

$$H_2NO_2^{\oplus}PF_6^{\ominus} + H_2O \rightleftarrows HNO_2 + H_3O^{\oplus}PF_6^{\ominus} \qquad (2b)$$

A third equilibrium involving molecular complex formation between polyalkylaromatics and nitrosonium ion has been recently demonstrated [3]. The equilibrium constant for such complex formation between pentamethylbenzene and nitrosonium

$$ArH + NO^{\oplus}PF_6^{\ominus} \rightleftarrows ArH --- NO^{\oplus}PF_6^{\ominus} \qquad (3)$$

ion is uncertain, but it is presumably unity or larger. Also it is known that the formation constant is larger for pentamethylbenzene than for mesitylene.

Finally, a variety of equilibria exist between the various nitrogen oxides and water. Some of the more important equilibria are shown in eq. 4a–4c.

$$HNO_3 + HNO_2 \rightleftarrows N_2O_4 + H_2O \qquad (4a)$$

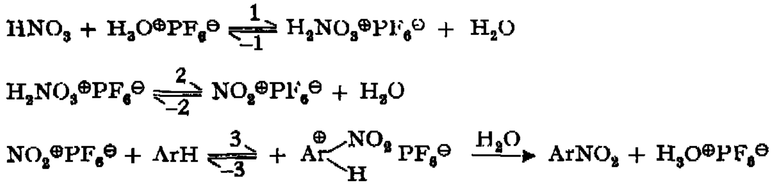
$$2HNO_2 \rightleftarrows N_2O_3 + H_2O \qquad (4b)$$

$$2N_2O_3 \rightleftarrows N_2O_4 + NO \qquad (4c)$$

In the ensuing discussion it will be necessary to refer to these four sets of equilibria and to emphasize their changing importance as the reaction progresses.

3.2. *Mechanistic Description of Stage I.* The first stage of the reaction has the characteristics of nitration by the nitronium ion with the condition that nitronium ion formation is rate-limiting. Thus the observations that benzene, mesitylene and pentamethylbenzene have the same initial rate of nitration under reference reaction conditions and the observation that changing the concentration of pentamethylbenzene by a factor of five does not change the rate of reaction indicate that the initial rate is zeroth-order in aromatic reactant.

Adopting the assumption that in nitromethane one equivalent of nitronium hexafluorophosphate and two equivalents of water yield nitric acid and hydronium hexafluorophosphate (eq. 1a and 1b), one can derive a rate expression that seems consistent with the first stage of the reference reaction profile. Following the conventional scheme,



$$HNO_3 + H_3O^{\oplus}PF_6^{\ominus} \underset{-1}{\overset{1}{\rightleftharpoons}} H_2NO_3^{\oplus}PF_6^{\ominus} + H_2O$$

$$H_2NO_3^{\oplus}PF_6^{\ominus} \underset{-2}{\overset{2}{\rightleftharpoons}} NO_2^{\oplus}PF_6^{\ominus} + H_2O$$

$$NO_2^{\oplus}PF_6^{\ominus} + ArH \underset{-3}{\overset{3}{\rightleftharpoons}} + \overset{\oplus}{Ar}\left\langle{}^{NO_2}_{H}\right. PF_6^{\ominus} \xrightarrow{H_2O} ArNO_2 + H_3O^{\oplus}PF_6^{\ominus}$$

One may write

$$\text{rate} = -d[ArH]/dt = \frac{k_1k_2k_3[ArH]\,[HNO_3]\,[H_3O^{\oplus}PF_6^{\ominus}]}{k_2k_3[ArH] + k_{-1}k_3[ArH]\,[H_2O] + k_{-1}k_{-2}\,[H_2O]^2} \tag{5}$$

where both $H_2NO_3^{\oplus}$ and $NO_2^{\oplus}$ are assumed to be steady-state intermediates and proton transfer from the σ-complex is assumed to be fast with respect to the reverse of step 3. Equation 5 reduces to the zeroth-order rate expression (eq. 6) if it is assumed that $k_{-1}k_3[ArH]\,[H_2O] \gg [k_2k_3[ArH] + k_{-1}k_{-2}[H_2O]^2]$.

$$\text{rate} = -d[ArH]/dt = \frac{k_1k_2}{k_{-1}} \cdot \frac{[HNO_3]\,[H_3O^{\oplus}PF_6^{\ominus}]}{[H_2O]} \tag{6}$$

The major characteristic of the reaction profile during stage 1 is the rapid fall-off in nitration rate. Equation 6 requires such a fall-off due to diminishing concentration terms in the numerator and a concentration term in the denominator that increases with extent of reaction.

In an effort to compare predictions with observations one can treat the more general rate equation (eq. 5) in a more detailed way. However, it must be recognized that this necessitates a number of serious assumptions. First, it is implicitly assumed that concentrations represent activities. Second, it is recognized that the term $k_{-1}k_{-2}\,[H_2O]^2$ in equation 5 cannot be neglected as the water concentration increases. This implies a gradual change from zeroth-order dependence in aromatic to a mixed order[7]. Third, it is assumed that step 3 and step 2 are controlled by encounter so that the rate constants k_3 and k_{-2} are approximately equal. Finally, we assume complete conversion of nitronium hexafluorophosphate and water to nitric acid and hydronium hexafluorophosphate, and also assume that equations 2a and 2b, governing the nitrosonium ion-nitrous acid equilibria, lie completely to the side of nitrosonium ion and water.

Application of the second and third assumptions leads to equation 7.

$$\text{rate} = -d[ArH]/dt = \frac{k'\,[ArH]\,[HNO_3]\,[H_3O^{\oplus}PF_6^{\ominus}]}{[ArH]\,[H_2O] + [H_2O]^2} \tag{7}$$

$$\text{where } k' = \frac{k_1k_2k_3}{k_{-1}k_3} \simeq \frac{k_1k_2k_3}{k_{-1}k_2}$$

---

[7] There is some experimental evidence to support this. Fig. 3 shows that the fall-off in the rate of nitration with time is less when the concentration of the aromatic reactant is increased.

By virtue of the known stoichiometry, the concentration of nitrosonium salt impurity (taken as 10% in the following treatment), and the assumptions concerning equilibria in equations 1 and 2, we may express the concentrations of equation 7 in terms of one variable.

Letting $[ArH]_0 = a$, $[ArH]_t = x$, $[H_3O^{\oplus}PF_6^{\ominus}] = 0.9a$

$[HNO_3]_t = (x - 0.1a)$, and $[H_2O]_t = 1.2a - x$, we obtain equation 8 upon substitution

$$-dx/dt = k' \frac{(x)\,(0.9a)\,(x - 0.1a)}{x\,(1.2a - x) + (1.2a - x)^2} = k' \frac{(0.9)\,(x)\,(x - 0.1a)}{1.2\,(a - x)}$$

Integration yields equation 9:

$$12 \log \frac{(0.9)\,(x/a)}{[(x/a) - 0.1]} + \log 1.11\,[(x/a) - 0.1] = \frac{0.9\,k't}{1.2} \tag{9}$$

A plot of the fraction of reactant remaining, x/a, *vs.* time (in units of 1/*k*) is shown in Fig. 8. The effect of adventitious water on this rate profile can also be estimated by appropriate changes in constant terms in equation 9. Results of similar calculations involving increased amount of water are included in Fig. 8.

For comparison purposes, experimental values of x/a from the standard reaction (Fig. 1) are also included.

The experimental curve was constructed by setting the experimental value of the time for x/a = 0.6 equal to the predicted value and adjusting the time axis of the other experimental x/a values accordingly. (This value was chosen for the basis as the experimental error in the time for 10% reaction (x/a = 0.9) is fairly large).

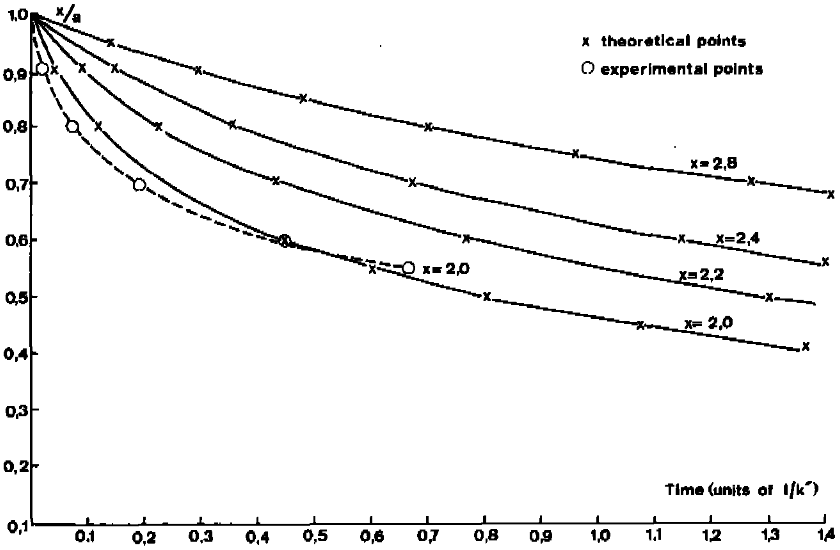


Fig. 8. *Theoretical Plot of the Fraction of Aromatic Reactant Remaining, x/a,* vs. *Time* (in units of 1/*k'*) *in the Nitration of Pentamethylbenzene* (1.0) *with Nitronium Salt* (0.9) *and Water* (X) (See Text)

In view of the assumptions made in deriving equation 7, the agreement between the predicted and experimental curves for stage I of the reaction is good. The observed rapid fall-off in nitration rate during stage I can be adequately described by the proposed mechanism.

The effect of water on stage I seems consistent with rate-limiting formation of the nitronium ion. The effects of other species on the zeroth-order nitration rate can be predicted from equations 1a and 1b. Thus a decrease or increase in the concentration of the nitronium ion or its precursor, the nitric acidium ion, would be expected to decrease or increase the initial rate of nitration, respectively. At first sight, the situation would appear to be similar to that found for zeroth-order nitrations with nitric acid in nitromethane. Here, nitration is anticatalyzed by dinitrogen tetroxide and catalyzed by sulfuric acid. The anticatalytic effect of dinitrogen tetroxide has been attributed to deprotonation of the nitric acidium ion by the nitrate ion, or in the presence of water, the nitrite ion [8]. The addition of dinitrogen tetroxide to the standard reaction of this study results in a decrease in the initial rate, presumably for the reasons mentioned above, but a quantitative evaluation of the anticatalysis is precluded by the changes which occur in equilibria 1–4 when dinitrogen tetroxide is added to the system.

In contrast to expectation, however, the addition of 99.2% sulfuric acid did not alter the initial rate of nitration. Furthermore, the addition of 96% sulfuric acid depressed the initial rate and initiated a reaction with characteristics similar to those shown by stage II of the standard system (Fig. 5). These results are disturbing. A number of possible explanations have been carefully considered. Many cannot be discounted, but in our judgement none is sufficiently convincing. We conclude that more detailed experimental work must be done before the effects of sulfuric acid can be adequately discussed.

The effects of adding sulfuric acid to the standard reaction system force us to be reserved about mechanistic assignment to stage I. The weight of evidence indicates zeroth-order nitration by the nitronium ion, but the sulfuric acid anomaly prevents adoption of a dogmatic position.

3.3. *Mechanistic Description of Stage II.* The observation that the onset of this reaction is favored by the addition of water or dinitrogen tetroxide provides clear evidence for the involvement of oxides of nitrogen. Production of nitrous acid during the reaction leads to autocatalysis, and the catalytic role played by nitric acid is supported by the observation that at the end of the reaction 10–20% pentamethylbenzene and *ca.* 20% nitrous acid are present in solution and the subsequent reaction is very slow.

The incursion of an autocatalytic reaction in the standard system can be accounted for by the changes which occur in the concentrations of the various species as reaction proceeds. With progression of stage I, the concentrations of the nitronium ion and pentamethylbenzene decrease, thereby increasing the availability of water (equilibrium 1a) and nitrosonium ion (equilibrium 3), respectively. The resulting shift in equilibrium 2a enhances the possiblity of formation of dinitrogen tetroxide. A time is thus reached where another nitration pathway, stage II, becomes important. With the onset of this reaction more nitrous acid is produced and nitric acid, released from equilibria 1a and 1b, acts as a catalyst.

The problem is to find a suitable mechanism or mechanisms, involving pentamethylbenzene and some form of nitrous acid, which will account satisfactorily for the characteristics shown by this reaction.

It is well known that reactive aromatic hydrocarbons are capable of undergoing conversion to nitro-compounds *via* nitrosation, and a number of species are capable of effecting both the nitrosation [12] and oxidation [13] stages of the reaction, depending on the conditions employed. In the system under discussion, the most reactive nitrosating agent is almost certainly the nitrosonium ion, but the lack of any reaction between this ion and pentamethylbenzene under anhydrous conditions necessitates the search for an alternative reaction path.

The preliminary experiments (Table 2) confirmed that pentamethylbenzene undergoes reaction to give pentamethylnitrobenzene and by-products in a system containing oxides of nitrogen. The data show clearly that the nitro-compound is formed principally from reaction of some species with the molecular complex formed between the aromatic reactant and the nitrosonium ion. The rapid decline in the rate of this reaction can be attributed to the attainment of a balance between equilibrium 3 and equilibria 2a, 2b, 4a, and 4b. It might be noted that the absence of an aldehyde is to be expected; the increased amount of nitrosonium salt decreases the amount of free water available for its formation.

More quantitative experiments involved an examination of the reactions of pentamethylbenzene and the molecular complex with dinitrogen tetroxide in nitromethane and acetonitrile. It is apparent from the results (Tables 3 and 4) that the reaction of the molecular complex with dinitrogen tetroxide shows similarities to stage II of the standard system. Both reactions are catalyzed by nitric acid and both produce a relatively high yield of pentamethylnitrobenzene. In contrast, the reaction without added nitrosonium salt is relatively slow and produces only a small amount of the nitro-compound. Since dinitrogen tetroxide can undergo heterolytic as well as homolytic decomposition, the formation of the molecular complex and its subsequent decomposition might participate in this reaction. For this reason it is difficult to estimate the contribution of the reaction of dinitrogen tetroxide (or nitrogen dioxide) with pentamethylbenzene to stage II of the standard reaction. This contribution is, in our opinion, likely to be small in view of the slow rate of reaction and the large amount of by-product formed.

We have not investigated the possibility that other oxides of nitrogen participate in stage II, but nitrogen trioxide is 80% dissociated into nitric oxide and nitrogen dioxide at 25° and atmospheric pressure [14], and the low reactivity of nitric oxide argues against its involvement in such a reaction.

Assuming, then, that the reaction between pentamethylbenzene, nitrosonium hexafluorophosphate and dinitrogen tetroxide provides a basis from which a plausible reaction scheme for stage II can be derived, we shall now consider the mechanism of this reaction in more detail. The reacting species have been identified as the molecular complex and nitrogen dioxide (Table 5 and Fig. 7). It is possible that the radical and the nitrosonium ion first react to form a species which then attacks pentamethylbenzene in a step which may be fast or slow compared to its rate of formation. *Raman* spectra of nitric acid solutions indicate the formation of a molecular compound between the nitrosonium ion and nitrogen dioxide [15], but of the two possible resonance structures, $NO^{\oplus}NO_2$ and $NO_2^{\oplus}\cdot NO$, the greater contribution comes from the nitrosonium-nitrogen dioxide ion [15].

The hypothesis that some species can be formed which attacks the aromatic in a separate step does not, however, find support from studies of the reactions of nitrogen dioxide with the complexes formed between the nitrosonium ion, pentamethylbenzene and mesitylene (Fig. 6). In the mesitylene case, the concentration of the molecular complex at equilibrium is smaller [3] thus affording the opportunity for the production of a larger amount of the attacking species. If the reaction were zeroth-order in aromatic reactant, mesitylene should react faster than pentamethylbenzene; in fact it reacts much slower.

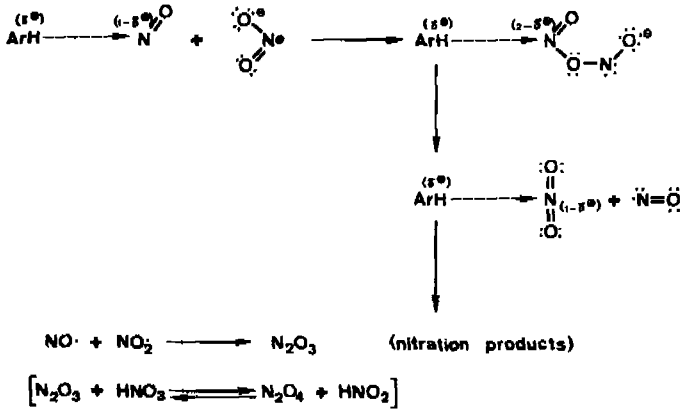
This result also argues against a first-order nitration of the aromatic hydrocarbon. Previous work [16] has shown that mesitylene acts at or near the encounter rate in nitrations with the nitronium ion in various media at 25°. The large difference observed in the rates of nitration of pentamethylbenzene and mesitylene under the present conditions does not therefore support the view that these compounds undergo a first-order nitration by a species formed between nitrogen dioxide and the nitrosonium ion. In our opinion this large difference in nitration rates is a direct consequence of the lower concentration and reactivity of the mesitylene complex towards nitrogen dioxide.

Alternatively, the reaction may be considered as a nitrosation-oxidation if one allows the possibility that a small amount of the σ-complex formed between the aromatic hydrocarbon and the nitrosonium ion is present in equilibrium with the molecular complex. Nitrosation by the nitrosonium ion is considered to be an A–S_E2 process in which proton loss from the *Wheland* intermediate is rate-limiting except for basic ($pK_a \geqslant -3.5$) compounds [17]. Thus in the present case nitrogen dioxide could catalyze the reaction by assisting proton removal from the σ-complex, but the absence of a kinetic isotope effect in the reaction effectively rules out this idea.

We must conclude that the rate equation, rate $= k_2$[complex][$NO_2\cdot$], describes a direct attack of nitrogen dioxide on the complex, and it is necessary to justify our earlier view that such a reaction can account satisfactorily for the characteristics shown by stage II of the standard system.

The reaction between the complex and nitrogen dioxide can be represented by the following scheme.

Scheme 1



It is a step-wise process in which donation of the lone pair of electrons from the nitrogen atom of the nitrosonium ion to an oxygen atom of a nitrogen dioxide molecule is followed by a reaction of the aromatic compound with the incipient nitronium ion and simultaneous release of nitric oxide. Undoubtedly the driving force of this reaction is the presence of the aromatic reactant, for in its absence the nitronium ion is not formed (see above). A possible alternative to the above scheme could involve a 1,3-cycloaddition of nitrogen dioxide to the nitrosonium ion of the complex followed by elimination of nitric oxide (compare [13]), but from the present results it is not possible to distinguish these two mechanisms.

The observation (Table 4) that nitric acid catalyses the reaction without appreciably altering the pentamethylnitrobenzene/by-product ratio is consistent with the idea that under these conditions the acid is not involved in the product-determining step of the reaction.

In stage II of the standard reaction, the initial concentration of nitrogen dioxide is small and catalysis by nitric acid is responsible for the fast rate of reaction. As the reaction progresses, the equilibrium concentration of the molecular complex is maintained by an appropriate shift in equilibrium (3). When no more nitric acid is present in the system, the reaction virtually stops with 10-20% pentamethylbenzene and *ca.* 20% nitrous acid unreacted.

A consideration of the reaction between the molecular complex and nitrogen dioxide can, therefore, lead to an adequate description of stage II, but there is an important difference between the two reactions, namely in the proportions of products formed. The former reaction gives *ca.* 80% pentamethylnitrobenzene on completion whereas in stage II *ca.* 50% of the nitrocompound and *ca.* 50% by-products are formed. Two explanations can be considered to account for the relatively low yield of nitro-compound in the second reaction. First, the proportion of by-product in the total yield may be increased by participation of a reaction between the aromatic reactant and nitrogen dioxide. Second, the reaction between the molecular complex and nitrogen dioxide may proceed *via* a mechanism which allows two distinct paths, one of which produces by-products and is accelerated under the conditions of stage II.

In view of the slow rate of the reaction between pentamethylbenzene and dinitrogen tetroxide (nitrogen dioxide) it is unlikely that this reaction can account for more than a small proportion of the by-products formed in stage II. There is, however, limited evidence to support the alternative view that the amount of by-product formed in the reaction of nitrogen dioxide with the molecular complex depends on the reaction conditions. Thus an increase in the concentration of complex at equilibrium by addition of two equivalents of nitrosonium salt increases the proportion of pentamethylnitrobenzene formed but only by a relatively small amount (Table 4). With five equivalents of nitrosonium salt (not shown in Table 4) the yield of nitrocompound decreased to its original value. This implies that some of the by-products are formed from reaction of the molecular complex. Furthermore, the observation that the yield of pentamethylnitrobenzene depended on the method used to dry the solvent, reaching a maximum with anhydrous material[6]), suggests that the proportion of by-product formed from the reaction of the molecular complex depends on the reaction conditions.

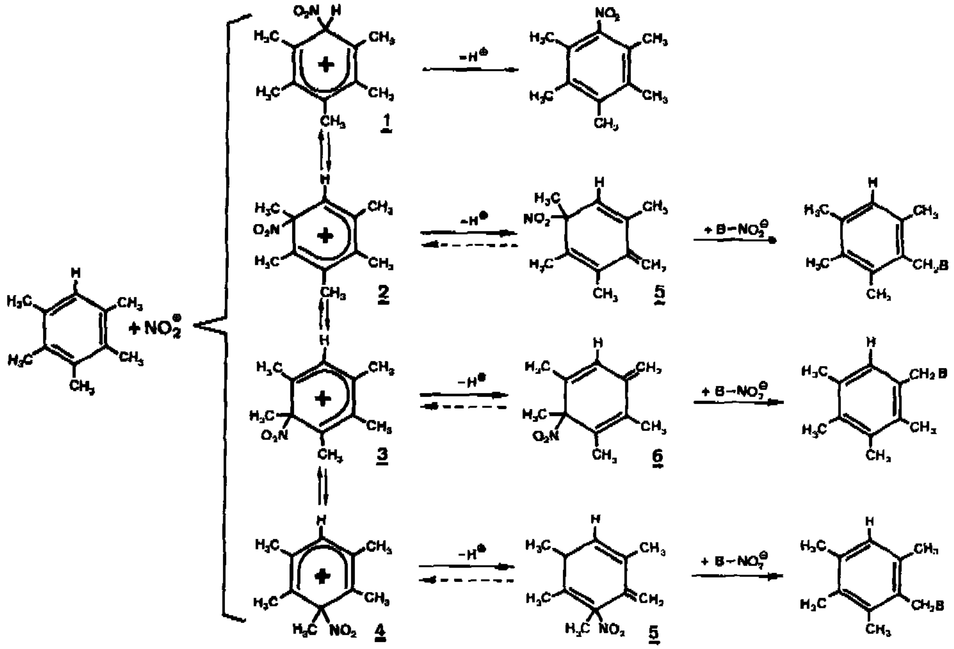
A mechanism to account satisfactorily for these observations can be derived if the possibility that the nitronium ion can attack aromatic carbon bearing a methyl group is considered (hereafter referred to as *ipso* positions [18]).

Earlier work [19] has shown that a consideration of these *ipso* complexes is necessary to explain certain aspects of aromatic nitration, particularly in the nitration of *o*-xylene. It could be shown that in the nitration of this compound with nitric acid in sulfuric acid *ca.* 40% reaction proceeded *via* the *ipso*-σ-complex, and this complex could undergo two modes of decomposition. At low sulfuric acid concentrations, a nucleophilic attack by water leads to the formation of 3,4-dimethylphenol, but at high acidities the predominant pathway involves a 1,2 shift of the nitro group to give the 3-nitro isomer. The observed [20] increase in the isomer ratio 3-/4-nitro-*o*-xylene with increasing acidity of the medium could thus be accounted for by the increasing predominance of the latter pathway.

In nitrations of pentamethylbenzene it must be assumed that reaction proceeds primarily *via* attack of the nitronium ion at the *ipso* positions. This consideration leads to the following mechanistic scheme for reaction of pentamethylbenzene with the nitronium ion and hence for reaction of the molecular complex with nitrogen dioxide.

The relative proportions of the σ-complexes formed will not be in the statistical order. Of the factors which govern their formation, two are expected to be of prime importance, namely the amount of steric strain released on formation of the complex and stabilization of the positive charge. In the case of the latter factor, the greatest stability is achieved when an electron-releasing group is present at the *para*-position; this position carries a larger proportion of the positive charge than an *ortho*- or *meta*-position [21]. Such considerations coupled with the statistical distribution lead to the conclusion that the *ipso* complexes will be formed in the proportion **3** > **2** > **1** > **4**.

Scheme 2



In the proposed scheme, it is envisaged that σ-complex **1** loses a proton from the position of substitution in a step which is fast compared to the rate of attack of the nitronium ion. The absence of a kinetic isotope effect in the reaction of the molecular complex ArH-NO$^{\oplus}$PF$_6^{\ominus}$ with nitrogen dioxide confirms this. Evidence from other work [6c] indicates that complex **1** does not undergo noticeable proton loss from a *para*-methyl group; such a process would lead to the formation of 2,3,4,6-tetramethyl compounds. For the other σ-complexes, two modes of decomposition, both fast compared to the initial attack of the nitronium ion, can be considered. First 1,2 shifts of the nitro group can occur to give **1** which then loses a proton to form pentamethylnitrobenzene. Second, loss of a proton from a methyl group *para* to the point of attack can lead to the formation of cyclohexadiene intermediates. In the case of **4** this process would, in all probability, give intermediate **5**. The formation of these conjugate bases would be base catalyzed, and their further reaction would lead to by-product formation.

It is immediately apparent from the present data that in stage I of the standard reaction the principal mode of decomposition of the σ-complexes involves 1,2-shifts of the nitro group. The small amounts of by-product and nitrous acid formed are consistent with the view that decomposition to give **5** and **6** occurs to a very small extent.

A similar situation obviously occurs in the reaction of the molecular complex and nitrogen dioxide in anhydrous nitromethane and acetonitrile. However, in stage II of the standard reaction, and in the reaction of the complex with nitrosonium salt and water, the increased availability of basic species (H_2O, $NO_3^\ominus$, $NO_2^\ominus$) increases the possibility that the σ-complexes decompose *via* intermediates **5** and **6**. The consequences of this situation are an increase in the concentration of nitrous acid in the system and an increase in the proportion of by-product formed.

A possible alternative to the above scheme could involve the formation of addition compounds by attack of a nucleophile ($B^\ominus$) on **2** and **3**. These addition compounds may then lose HB to give **5** and **6** or eliminate nitrous acid to give products capable of undergoing rearrangement [5]. Other possible paths of decomposition could involve intermediate benzyl cations. These may be formed either from **2** and **3** by a concerted elimination of nitrous acid or from **5** and **6** by loss of nitrite ion.

In our opinion, however, *scheme 2* provides a reasonable explanation for the observations reported here and can account satisfactorily for the changes in product proportions which occur under the various reaction conditions.

With regard to the nature of the species which react with **5** and **6** to form the by-products in stage II, the present results do not allow a distinction between a radical or ionic process. The relatively large amount of by-product formed in this reaction compared to the amount of nitrous acid produced is suggestive of a reaction involving nitrogen dioxide, but it is clear that the by-products can be formed in a number of ways and are capable of further reaction in the system. Their nature is of relative unimportance to the general theme of this account.

To summarize, the general mechanistic characteristics of the standard reaction have been established. Both stage I and stage II involve nitration by the nitronium ion. In stage I, the nitronium ion is released from equilibrium 1a whereas in stage II it is formed from the interaction of nitrogen dioxide with the molecular complex formed between pentamethylbenzene and the nitrosonium ion. Both reactions proceed *via* *ipso*-σ-complexes, and pentamethylnitrobenzene is formed by 1,2-shifts of the nitro group followed by proton loss from the conventional σ-complex. In stage II, however, a base catalyzed proton loss from a methyl group *para* to the point of attack can compete with the shift of the nitro group owing to the increased availability of basic species. Further reaction of the cyclohexadiene intermediates leads to by-products. Finally, some of the by-products in stage II may be formed by an attack of dinitrogen tetroxide (nitrogen dioxide) on pentamethylbenzene.

In the final section we shall consider the reactions of pentamethylbenzene in various nitration systems and investigate the possibility of the emergence of a clear pattern of behavior.

3.4. *Related Nitration Systems.* The results obtained in the present work for the nitrations of pentamethylbenzene with fuming nitric acid in nitromethane and acetonitrile (Table 6) are suggestive of a radical reaction. Thus the product distributions are similar to that in the reaction of the aromatic hydrocarbon with dinitrogen tetroxide in nitromethane (Table 2) and furthermore, gas-chromatography shows qualitatively that similar by-products are formed. However, other workers who have studied the nitration of pentamethylbenzene with fuming nitric acid in nitromethane have claimed that the purported high positional selectivity of the reaction which forms the by-products, *i.e.* side-chain nitrooxylation argues against the participation of a radical reaction [7]. In view of the fact that fuming nitric acid contains *ca.* 1% dinitrogen tetroxide which can undergo heterolytic and homolytic dissociation, a reaction between the molecular complex and nitrogen dioxide is possible under these conditions. The reaction would be catalyzed by nitric acid and, for the reasons outlined in the previous section, the relatively high concentration of basic species compared to that of the molecular complex would favor by-product formation. Thus nitration *via* the nitronium ion could occur in this system, but it is clear that the reaction does not involve nitration *via* nitronium ion produced from the dissociation of nitric acid (see Introduction)[8].

In nitromethane, addition of sulfuric acid to the system results in an increase in the reaction rate and in the proportion of pentamethylnitrobenzene formed on completion (Table 6). These observations are consistent with the view that sulfuric acid increases the concentration of the nitronium ion in the system by protonating nitric acid, and also decreases the basicity of the medium. Under these conditions nitration *via* the nitronium ion formed from nitric acid occurs, and the decreased basicity of the medium favors decomposition of the *ipso*-σ-complexes *via* 1,2-shifts of the nitro group.

The situation is, however, not found when the solvent is changed to acetonitrile. The rate of the reaction is increased by addition of sulfuric acid, but this increase in rate is not accompanied by a large increase in the proportion of pentamethylnitrobenzene formed; a similar situation has been found with durene [3]. If it is assumed that, in the presence of two equivalents of sulfuric acid, nitration *via* the nitronium ion formed from nitric acid occurs, the high proportion of by-product formed in the nitration must be a consequence of the predominance of the corresponding mode of decomposition of the *ipso*-σ-complexes. The existence of an inverse partition isotope effect in the reaction (Table 7) supports this interpretation; substitution of deuterium for hydrogen in an α-methyl group of pentamethylbenzene decreases the possibility that the *ipso*-σ-complex will decompose *via* proton loss to form a cyclohexadiene intermediate.

The differences observed between the mixed acid nitrations in nitromethane and acetonitrile must be due to the ability of acetonitrile to act as a nucleophile towards the small equilibrium concentration of the cyclohexadiene intermediates, and hence accelerate the decomposition pathway of the *ipso*-σ-complexes which leads to by-products.

Nucleophilic attack by the solvent occurs in the nitration of pentamethylbenzene with nitronium salts in acetonitrile [3] and there is some evidence to suggest that it occurs in the nitration with mixed acid. In this system, attack by the solvent on intermediates **5** and **6** (*scheme 2*) would form N-acetyltetramethylbenzylamines whose presence is indicated by the infrared spectrum of the products.

It is quite clear therefore that the conditions used to study the nitration of pentamethylbenzene can have a large effect on the proportions of the products formed. It is also clear that many of the factors which influence the nitration of this com-

---

[8] Less reactive hydrocarbons *e.g.* benzene which do not form a significant amount of the complex $ArH\text{-}NO^{\oplus}PF_6^{\ominus}$ under these conditions undergo nitration *via* the nitronium ion produced from the dissociation of nitric acid. With fuming nitric acid (1.0 M) in nitromethane, the reaction is zeroth-order with respect to benzene, $k_0 = ca.\ 1.0 \times 10^{-6}$ mol l^{-1} s^{-1}.

pound are effective in the nitrations of other alkylbenzenes. Thus the observation [22] of red-brown colors in nitrations of aromatic hydrocarbons in acetic acid is indicative of the molecular complexes formed between these compounds and the nitrosonium ion, and in view of the possibility of reaction of these complexes with nitrogen dioxide care must be exercised in experiments designed to measure relative reactivities of these aromatic hydrocarbons. The reaction of these molecular complexes with nitrogen dioxide can also account satisfactorily for the surprising observation [23] that dinitrogen tetroxide nitrates aromatic hydrocarbons cleanly and in high yield. The results are explainable if it is the complex and not the aromatic hydrocarbon which undergoes reaction with nitrogen dioxide under the conditions employed.

In this account we have attempted to elucidate the general principles which govern the nitration of pentamethylbenzene and other polyalkylbenzenes, and hence to establish why the nature and proportions of the products formed in these nitrations which are not affected by the mixing process vary so much with the nature of the system used to study nitration. The mechanistic *schemes 1* and *2* provide in our opinion, a basis from which a plausible explanation of these observations can be made. Thus in media in which the concentration of the nitronium ion relative to that of nitrous acid is high enough to ensure that nitration *via* the nitronium ion occurs exclusively, pentamethylbenzene undergoes reaction to give only pentamethylnitrobenzene, *e.g.* stage I of the standard reaction of this study. However, in such nitrations the formation of by-products can occur if conditions are such to increase the probability of the formation and further reaction of methylene cyclohexadiene intermediates, *e.g.* mixed acid in acetonitrile. In systems which have a relatively high concentration of nitrous acid, an oxidation-nitration reaction can occur which appears to involve attack by nitrogen dioxide on the molecular complex $ArH{-}NO^{\oplus}PF_6^{\ominus}$ and reaction of the incipient nitronium ion with the aromatic substrate. This reaction can give up to 85% pentamethylnitrobenzene, but usually the very nature of the nitration systems in which it takes place ensures that considerable decomposition of the *ipso*-σ-complexes occurs *via* methylene cyclohexadiene intermediates, *e.g.* stage II of the standard reaction of this study, and possibly nitration with fuming nitric acid in organic solvents. Finally, reaction between pentamethylbenzene and nitrogen dioxide may occur under certain conditions, *e.g.* nitration with fuming nitric acid in organic solvents.

We thank the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* for financial support (project No. 2.245.69).

4. Experimental Part. – *Material and Analytical Methods.* Commercial pentamethylbenzene was fractionated five times (65°/0.05 Torr) and recrystallized from ethanol, m.p. 54°. Gas-chromatography, showed less than 0.01% durene and hexamethylbenzene. Benzene and mesitylene (*Merck*, pure) were distilled. 2,3,4,5-Tetramethylbenzyl chloride was prepared by chloromethylation of prehnitene [24]. The corresponding nitrate and aldehyde were prepared from this compound by standard methods [6c]. 2,3,4,5-Tetramethylbenzyl alcohol was isolated from the nitration of pentamethylbenzene (2M) with fuming nitric acid (7M) in chloroform by column-chromatography (silica gel; diethylether) and recrystallized twice from 60–80° petroleum ether. The physical properties and spectral-characteristics of these compounds agreed with those reported in the literature.

Acetonitrile (*Fluka*, pure) was fractionally distilled three times from P_2O_5 in a dry nitrogen atmosphere. The final sample was inert to *Fischer* reagent. Dimethylformamide (DMF) (*Fluka*, spectroscopic grade) was shaken for 12 h with 4A molecular sieves and fractionally distilled from P_2O_5. Fuming nitric acid (d = 1.52) containing 1% nitrous acid, and sulfuric acid (d = *ca.* 1.84, 95.7%) were from *Merck*. Dinitrogen tetroxide was a commercial product and was dried by passage over P_2O_5. The purification of other materials and the determination of nitrous acid have been described [3].

An *Aerograph* series 1400 (flame ionisation detector; 200°; 30 ml/min N_2) was used for the GLC. analyses. The column has been described [2]. Naphthalene was the internal standard. ^{1}H-NMR. spectra were recorded on a *Varian* A60 or HA100 spectrometer. IR. spectra were obtained with a *Perkin-Elmer* 21 spectrophotometer. A *Hitachi-Perkin Elmer* RMU-6A mass spectrometer was used to obtain the mass spectral data. Kinetic measurements were carried out with a *Unicam* SP 800 spectrophotometer fitted with a thermostated cell block and equipped to record four kinetic runs simultaneously.

Pentamethylbenzene-1-d. The principle of the method has been described [25]. D_2O (6 ml) was added dropwise from a separating funnel to phosphorous tribromide (27 g) contained in a 50 ml two-necked, round-bottomed flask equipped with a magnetic stirrer. The gas evolved was collected as a solid at −180° in a flask containing pentamethylbenzene (3 g). The flask was connected *via* a three way tap to a $CaCl_2$ drying tube. When the evolution of DBr had ceased, the liquid nitrogen bath was exchanged for a dry ice/isopropyl alcohol bath whereupon DBr melted and dissolved the aromatic. After a reaction time of 30 min, the cooling bath was removed and the gas pumped off. The procedure was carried out twice more. Chromatography of the crude product (silica gel; benzene) showed the presence of a minor impurity, possibly pentamethylbromobenzene. Pentamethylbenzene-1-d_1 was purified by column-chromatography and was recrystallized from ethanol; 2.5 g, m.p. 54°. ^{1}H-NMR. and mass spectrum showed 100% replacement of the aromatic proton. An unlabelled sample was prepared from pentamethylbenzene and HBr.

Pentamethylbenzene-1-α-d_2. Sodium borodeuteride (0.61 g) was added to 2,3,4,5-tetramethylbenzyl chloride (1.5 g) in dry DMF (30 ml) contained in a 100 ml conical flask fitted with a drying tube. After a reaction time of 1 h, the solution was extracted with 30–50° petroleum ether (4 × 50 ml) and the extract concentrated to a volume of *ca.* 30 ml. This caused separation of most of the DMF which was soluble in the original extract. The DMF layer was separated and re-extracted with petroleum ether (2 × 10 ml). Chromatography showed that this was sufficient to extract the aromatic compound completely. The petroleum ether extracts were combined and concentrated to a small volume. Isolation and purification of pentamethylbenzene-α-d_1 was achieved by column-chromatography (silica gel; petroleum ether) and recrystallization from ethanol; 1.15 g, m.p. 53°. MS. showed 90 ± 2% deuteration. An unlabelled sample was prepared from sodium borohydride and the chloride. Gas-chromatography showed the samples to contain hexamethylbenzene (4.5%) impurity. Both samples were deuterated in the 1-position by the method described above.

Pentamethylnitrobenzene-α-d_1. This was isolated from the reaction of pentamethylbenzene-α-d_1 (0.2 M), nitrosonium hexafluorophosphate (0.2 M) and dinitrogen tetroxide (*ca.* 0.5 M) in nitromethane (see below). It was purified by chromatography (silica gel; petroleum ether/benzene 2:1) and recrystallization from methanol, m.p. 156°. An unlabelled sample was prepared in an analogous manner.

Nitration of Pentamethylbenzene with Nitronium Hexafluorophosphate and Water in Nitromethane. – A. *Kinetic Studies.* The method used was essentially that described previously for nitrations without water [3]. Solutions of the aromatic and of the nitronium salt were prepared in a dry box. The latter solution was removed from the box, the required amount of water was added with a syringe and the solution returned to the box. Equal volumes (usually 3 ml) of the two solutions were pipetted into the side arms of V-tubes; these were stoppered and removed from the dry box. After equilibration at the required temperature, the tubes were inverted and the solutions thoroughly mixed. The contents of each tube were quenched with ammonia gas at various times from the start of the reaction and the solutions filtered. Samples of each solution were added to samples of a naphthalene solution of known concentration and the extent of nitration was determined by gas-chromatography using the experimentally determined response factors. Exactly the same procedure was used to study the nitrations of benzene and mesitylene, but solutions of the aromatic in nitromethane were prepared by adding an appropriate amount of the hydrocarbon to the solvent by means of a syringe.

B. *Products.* The experimental procedure has been described above. A solution (100 ml) of the nitronium salt (0.05 M) and water (0.1 M) was added to a solution (100 ml) of pentamethylbenzene (0.05 M) contained in a 500 ml conical flask in a dry box at 20.5°. The extent of reaction was followed by gas-chromatography, and it was established that the course of the reaction was similar to those studied previously, see Fig. 1. After a reaction time of 25 min, the solution was quenched with ammonia gas and filtered. Gas-chromatography showed the presence of pentamethylnitrobenzene (61%), pentamethylbenzene (23%) and 2,3,4,5-tetramethylbenzaldehyde (1.5%). The solution was concentrated and the residue dissolved in chloroform (20 ml). The IR. spectrum showed bands at 2930 cm^{-1} (C—H str.), 1690 cm^{-1} (C=O str.), 1520 cm^{-1} (N—O str.), 1460 cm^{-1} (C=C str.), and 1375 cm^{-1} (N—O str.). A number of other bands were observed, but no definite assignments could be made. Part (5 ml) of the solution was evaporated to dryness and the residue dissolved in the minimum of deuterochloroform. The ^{1}H-NMR spectrum showed peaks at 2.1, 2.16, 3.87, 6.2 and 6.8 ppm. The remainder of the solution was concentrated and TLC. (silica gel; several solvent systems) showed the presence of at least ten by-products. Of these, two were isolated and purified by chromatography (silica gel; petroleum ether/benzene 2:1):

2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane: m.p. 180°. IR. ($CHCl_3$): 2930 cm^{-1} (CH_3, C—H str.), 1470 and 1450 cm^{-1} (benzene ring overtones and aromatic C=C str.), 1390 cm^{-1} (CH_3, C—H bend), and 1070 cm^{-1}. ^{1}H-NMR[9]) ($CDCl_3$): all singlets, 2.12 (9, arom. CH_3); 2.2 (3, arom. CH_3); 2.28 (12, arom. CH_3); 2.36 (3, arom. CH_3); 3.92 (2, CH_2); and 6.24 ppm (1, CH). MS.: M^+ at *m/e* 294.

2,3,4,5-tetramethylbenzaldehyde: IR. ($CHCl_3$): 2930, 2860 and 2720 (—CHO), 1690 (C=O), 1600, 1450, 1390, 1280, 1220, and 1080 cm^{-1}. Unfortunately too little of this compound was isolated to obtain the ^{1}H-NMR. spectrum.

Reaction of Pentamethylbenzene with Nitrosonium Hexafluorophosphate and Water in Nitromethane. – The reactions were carried out in the manner described above for reactions with nitronium salts. In the case of the reaction of the complex $ArH—NO^{\oplus}PF_6^{\ominus}$ with nitrosonium salt and water, the solution of the complex was prepared in a dry box by mixing equal volumes of nitromethane solutions of the aromatic (0.2 M) and the salt (0.2 M), and an aliquot was reacted with an equal volume of a nitromethane solution of the salt (0.1 M) and water (0.2 M) in a stoppered V-tube at 20°. The reaction was stopped with ammonia gas and analysed by gas chromatography.

Reaction between Pentamethylbenzene, Nitrosonium Hexafluorophosphate and Dinitrogen Tetroxide. – A. *Kinetic Studies in Nitromethane.* A quantity of the solvent was pipetted into a three-necked, round-bottomed flask in a dry box. Two of the necks were capped with rubber septums and the third was fitted with a tap attached to a balloon filled with dry nitrogen. A hollow, stainless steel needle was inserted through each septum and a short length of polythene tube, fitted with a screw clip, was fixed to one of the needles. The apparatus was removed from the box and dinitrogen tetroxide was bubbled through the solvent for a short time. Samples of the solution were removed by inserting a pipette into the tube attached to one of the needles and applying a little nitrogen pressure. In this way losses of the gas from the solution were minimized. The concentrations of dinitrogen tetroxide solutions prepared in this manner were determined as follows: An aliquot of the solution was added to excess of a standard solution of acidified potassium permanganate, the solution was stirred for 5 min and the permanganate remaining was determined iodometrically. The reactions between the aromatic, nitrosonium salt, and dinitrogen tetroxide were carried out in a separating funnel (3.5 × 17 cm) containing a magnetic stirrer. A nitromethane solution of the complex was prepared (see above) and added to the separating funnel in a dry box. The funnel was sealed with a rubber septum through which were inserted two stainless steel needles. One was connected *via* a three way tap to a drying tube and a balloon

---

[9]) The number in brackets refers to the number of protons.

filled with dry nitrogen; the other had attached to it a short length of tube sealed by a screw clip. The complete apparatus was removed from the box and thermostatted by means of a hollow lead pipe around the funnel and connected to a thermostat. A pipette containing the required volume of a solution of dinitrogen tetroxide in nitromethane was inserted into the tube equipped with the screw clip. The clip was opened and the contents of the apparatus were exposed to dry air. After addition of the dinitrogen tetroxide solution, the reaction mixture was subjected to a slight pressure of dry nitrogen to facilitate the running out of samples. These were taken at various times from the start of the reaction and run into tubes containing ammonia gas. After filtration, the samples were examined by gas chromatography.

The reaction of dinitrogen tetroxide with pentamethylbenzene was carried out in a similar manner.

B. *Kinetic Isotope Effect in Nitromethane.* Pentamethylbenzene (0.148 g) and pentamethylbenzene-1-d_1 (0.149 g) were weighed out in a 25 ml tube. The stoppered tube was put in a dry box and nitromethane (10 ml) was added. A solution of nitrosonium hexafluorophosphate (8 ml, 0.2 M) was added to part (8 ml) of the solution of aromatics to form the molecular complexes. The complex solution was removed from the box and reacted with a nitromethane solution of dinitrogen tetroxide (0.42 ml, 0.2 M) for 12 min. After being quenched with ammonia gas, the solution was filtered and part was examined by gas-chromatography while the remainder was evaporated to dryness. The unreacted hydrocarbons were separated from the products by chromatography (silica gel; 30–50° petroleum ether) and recrystallized from ethanol.

The remainder (2 ml) of the solution of aromatics not reacted with the nitrosonium salt was subjected to the same work up procedure and both samples were examined by mass spectroscopy.

C. *Kinetic Studies in Acetonitrile.* Preliminary work showed that a kinetic study of the reaction of the complex with dinitrogen tetroxide could possibly be complicated by the reaction of the complex with atmospheric moisture unless such conditions were employed to eliminate or compensate for this side reaction. Thus when a solution of the complex (0.0025 M) in dry ($< 4.0 \times 10^{-4}$ M H_2O) acetonitrile was prepared in a 1 cm cell in a dry box and then exposed to the atmosphere at room temperature for 30 s, decomposition of the complex set in ($t\,^1/_2 = ca.$ 40 min). Under the strictly anhydrous conditions of the dry box, the complex was completely stable. Further experiments showed that at 5° this decomposition would not interfere with measurement of the reaction with dinitrogen tetroxide if the following procedure were employed. A typical run is described: A solution of the complex (0.005 M) in dry acetonitrile was prepared in a dry box and aliquots (1.5 ml) were pipetted into two 1 cm matched quartz cells. The stoppered cells were transferred to the reference and sample compartments of the spectrophotometer and equilibrated at 5° for 10 min. A solution of dinitrogen tetroxide (0.142 M) in acetonitrile was prepared (see above) and was equilibrated at 5° together with a quantity of the solvent contained in a similar apparatus. After equilibration, a 1.5 ml aliquot of the solvent was added to the complex solution in the sample cell using the method described above for dinitrogen tetroxide solutions. Similarly, a 1.5 ml aliquot of the dinitrogen tetroxide solution was added to the reference cell. The solutions were quickly mixed and the decrease in the concentration of the complex was recorded at 500 nm.

The same two stock solutions of the complex and dinitrogen tetroxide were used in all kinetic runs. Different concentrations of dinitrogen tetroxide were achieved by the addition of aliquots of solvent to the initial 1.5 ml aliquots of the complex solutions contained in the two 1 cm cells; the total volume of the complex plus dinitrogen tetroxide solutions was always 3 ml. Between kinetic runs, the apparatus containing the dinitrogen tetroxide solution and that containing the solvent were kept in a dry box.

Nitration of Pentamethylbenzene with Nitric Acid and Sulfuric Acid in Nitromethane and Acetonitrile. – A. *General Method.* Solutions of pentamethylbenzene, fuming nitric acid and sulfuric acid were prepared by weight. The required amounts of material were weighed out in separate tubes. These were put in a dry box and the appropriate amount of dry solvent was added to the tubes containing the aromatic and nitric acid; an aliquot of the nitric acid solution was then added to the tube containing sulfuric acid. The tubes were then removed from the box and after equilibration at the required temperature part of the nitric acid/sulfuric acid solution was added to the solution of the aromatic reactant to give the required concentration and stoichiometry of reactants (see Table 6). The reactions were stopped with ammonia gas and examined by gas-chromatography.

B. *Kinetic Isotope Effect in Acetonitrile.* An acetonitrile solution (4 ml) of fuming nitric acid (0.02 M) and sulfuric acid (0.04 M) was added to a solution (4 ml) of pentamethylbenzene (0.1 M) and pentamethylbenzene-1-d_1 (0.1 M), and the reaction was left for 6 h at 20°. After being quenched with ammonia gas, part of the solution was examined by gas-chromatography and the remainder was evaporated to dryness. The unreacted hydrocarbons were separated by chromatography (silica gel; 30–50° petroleum ether) and examined by mass spectroscopy together with a sample which had not been reacted with the nitrating agent.

C. *Partition Isotope Effect in Acetonitrile.* To a solution (2 ml) of pentamethylbenzene-1-d_1 (0.09 M) and pentamethylbenzene-1-α-d_2 (0.09 M) was added a solution (2 ml) of fuming nitric acid (0.22 M) and sulfuric acid (0.44 M). After 10 h at 20° the reaction was stopped with ammonia and part of the solution was examined by gas-chromatography. Pentamethylnitrobenzene and pentamethylnitrobenzene-α-d_1 were isolated by chromatography of the remainder (silica gel; petroleum ether/benzene 3:1) and their ratio determined by mass-spectroscopy. A sample (1:1) of the nitrocompounds was put through the same work up procedure and used for comparison purposes.

REFERENCES

[1] *E. Baciocchi & G. Illuminati,* Prog. phys. org. Chemistry *5,* 1 (1967).

[2] *S. B. Hanna, E. Hunziker, T. Saito & H. Zollinger,* Helv. *52,* 1537 (1969).

[3] *E. Hunziker, J. R. Penton & H. Zollinger,* ibid. *54,* 2043 (1971).

[4] *E. Baciocchi, A. Ciana, G. Illuminati & C. Pasini,* J. Amer. chem. Soc. *87,* 3953 (1965).

[5] *R. Astolfi, E. Baciocchi & G. Illuminati,* La Chimica e l'Industria *53,* 1153 (1971), and references therein.

[6] *H. Suzuki,* (a) Bull. chem. Soc. Japan *43,* 481 (1970); (b) 879; (c) with *K. Nakamura,* 473; (d) idem ibid. *44,* 227 (1971).

[7] *K. Nakamura,* ibid. *44,* 133 (1971).

[8] *E. D. Hughes, C. K. Ingold & R. I. Reed,* J. chem. Soc. *1950,* 2400.

[9] *T. F. Redmond & B. B. Wayland,* J. phys. Chemistry *72,* 1626 (1968).

[10] *C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. M. Jacobs, M. H. Jones, G. J. Minkoff & R. I. Reed,* J. chem. Soc. *1950,* 2628.

[11] *R. W. Adler, G. R. Chalkley & M. C. Whiting,* Chem. Commun. *1966,* 405.

[12] *E. D. Hughes, C. K. Ingold & J. H. Ridd,* J. chem. Soc. *1958,* 58, 65, 70, 77, 82, 88.

[13] See for example *T. G. Bonner & R. A. Hancock,* J. chem. Soc. (B) *1970,* 519.

[14] *I. R. Beattie & S. W. Bell,* J. chem. Soc. *1957,* 1681.

[15] *J. D. S. Goulden & D. J. Miller,* ibid. *1950,* 2620.

[16] *S. R. Hartshorn, R. B. Moodie, K. Schofield & M. J. Thompson,* J. chem. Soc. (B) *1971,* 2447.

[17] *B. C. Challis & A. J. Lawson, J. C. S. Perkin II, 1973,* 918 and references therein.

[18] *C. L. Perrin & G. A. Skinner,* J. Amer. chem. Soc. *93,* 3389 (1971).

[19] *P. C. Myhre,* ibid. *94,* 7921 (1972).

[20] *R. G. Coombes & L. W. Russell,* J. chem. Soc. (B) *1971,* 2443.

[21] *G. A. Olah,* Accounts chem. Res. *4,* 240 (1971).

[22] *D. T. Clark & D. J. Fairweather,* Tetrahedron *25,* 5525 (1969).

[23] *G. R. Underwood, R. S. Silverman & A. Vanderwalde, J. C. S. Perkin II, 1973,* 1177.

[24] *F. Bennington, R. D. Morin & L. C. Clark,* J. org. Chemistry *23,* 2034 (1958).

[25] *Y. R. Kalinachenko, Ya. M. Varshavskii & A. I. Shatenshtein,* Dokl. Akad. Nauk SSSR *91,* 577 (1953); Chem. Abstr. *49,* 12094a (1955).