990. *Some Aspects of the Nitration of the Mononitrotoluenes.*

By J. G. Tillett.

The rate of nitration of *m*-nitrotoluene in aqueous sulphuric acid at 25° has been determined as a function of solvent composition over the range 72—87% w/w sulphuric acid. It has been established that a minor product (~1·4%) of the nitration is 3,5-dinitrotoluene. The relative rates of nitration of the three mononitrotoluenes have been measured by the competitive method. Orientation data for the nitration of the mononitrotoluenes are compared with values predicted by the additivity principle.

Chloromethylation of *m*-nitrotoluene is reported[1] to occur to some extent in the 5-position, *i.e.*, to give 3-chloromethyl-5-nitrotoluene. Similarly,[2] nitration of *m*-nitro-t-butylbenzene gives mainly the 3,4-, with a little 3,5-dinitro-t-butylbenzene. By analogy, it would be expected that nitration of *m*-nitrotoluene should yield at least some 3,5-dinitrotoluene and calculations based on the additivity principle indicate[3] that the 3,5-dinitro-isomer should form some 22% of the products. Gibson, Duckham, and Fairbairn, however, recorded[4] only the presence of the 3,4-, 2,3-, and 2,5-dinitro-isomers in the product. Since their analysis was made by comparison of the melting point of the crude product with those of ternary mixtures of the three isomers indicated, it seemed possible that the other isomer might be in the product. We have, therefore, re-examined the nitration of *m*-nitrotoluene, developing for the 3,5-dinitro-product a delicate quantitative test which can be used even in the presence of a large excess of the 3,4-dinitro-isomer which is the predominant product.

It has been established[5-7] that in many cases the rates of nitration of aromatic compounds are correlated with the J_0 acidity function rather than the H_0 acidity function. This has been interpreted as providing further evidence that the active nitrating agent is the nitronium ion itself rather than its hydrated form, the nitric acidium ion. A distinction cannot be made between the two possible reagents on kinetic grounds alone since reactions involving the electrophilic reagents X^+ and XOH_2^+ give identical kinetic equations for substitution reactions in dilute aqueous solution. If, however, the formation of these two reagents is considered, the reactions of the types shown in eqns. (1) and (2) are considered to follow the J_0 and H_0 acidity functions, respectively, and hence a distinction between the reagents is formally possible. The correlation with acidity of the rate of nitration of *m*-nitrotoluene has been investigated by determining the rate of nitration as a function of solvent composition over the range 72—87% w/w sulphuric acid.

$$XOH + H^+ \rightleftharpoons X^+ + H_2O \qquad (1)$$

$$XOH + H^+ \rightleftharpoons XOH_2^+ \qquad (2)$$

m-Nitrotoluene has been found to be intermediate in reactivity (for nitration) between (*a*) fairly reactive benzene and chlorobenzene and (*b*) relatively unreactive nitrobenzene. The range of acid concentration over which the rate of nitration of *m*-nitrotoluene has been studied overlaps the regions of acid concentration in which the rates of both chlorobenzene[7] and nitrobenzene[5] have been measured. Thus, by using a stepwise procedure the rates of nitration of *m*-nitrotoluene and nitrobenzene relative to benzene can be calculated. By using these relative rates in conjunction with the observed isomer ratios, partial rate factors have been obtained for the nitration of the mononitrotoluenes.

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[1] Matsukawa and Shirakawa, *J. Pharm. Soc. Japan*, 1950, **70**, 25.
[2] Ayad and Garwood, *Chem. and Ind.*, 1957, 1073.
[3] de la Mare, *Chem. and Ind.*, 1957, 1419.
[4] Gibson, Duckham, and Fairbairn, *J.*, 1922, **121**, 270.
[5] Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871.
[6] Lowen, Murray, and Williams, *J.*, 1950, 3318; Williams and Lowen, *J.*, 1950, 3312.
[7] Deno and Stein, *J. Amer. Chem. Soc.*, 1956, **78**, 578.

EXPERIMENTAL

Materials.—The mononitrotoluenes were commercial materials. They were fractionated or recrystallised before use and their purities were checked by gas-chromatography. A sample of *m*-nitrotoluene prepared [8] from carefully purified 2-nitro-*m*-toluidine was identical with the purified commercial sample and contained no other isomer.

3,4-Dinitrotoluene was a recrystallised commercial sample, m. p. 60° (lit.,[9] 59·5°). 3,5-Dinitrotoluene, on repeated recrystallisation from light petroleum (b. p. 60—80°), had m. p. 90° (lit.,[10] 92°) and was prepared from *p*-toluidine through acetyl-*p*-toluidine to *N*-acetyl-3,5-dinitro-*p*-toluidine (cf. ref. 10): this was hydrolysed to 3,5-dinitro-*p*-toluidine in boiling alcohol,[11] deamination [12] completing the sequence. 2,3- and 2,5-Dinitrotoluene were prepared from *o*-toluidine: acetylation with acetic anhydride followed by nitration and steam-distillation [13] gave 5- and 3-nitro-*o*-toluidine which were converted into 2,5-, m. p. 50° (lit.,[9] 48°), and 2,3-dinitrotoluene, m. p. 59° (lit.,[9] 59°), respectively.

" AnalaR " nitric acid (*d* 1·5) and sulphuric acid (B.D.H.; *d* 1·84) were used for nitrations. Their concentrations were determined by titration with standard alkali.

Kinetic Measurements.—The rate of nitration of *m*-nitrotoluene in aqueous sulphuric acid was followed spectrophotometrically. *m*-Nitrotoluene has $\varepsilon_{\text{max.}}$ (in water) 6900 at 274 mμ, whereas its nitration product (a mixture of the dinitrotoluenes) has a shallow maximum at 266 mμ ($\varepsilon_{\text{max.}}$ 5900). It was assumed that after the reaction had been stopped by addition of the mixture to water the resulting solution contained only these two absorbing species, since the absorption of nitric acid in this region of the spectrum is negligible.[14] Fig. 1 shows the absorption spectra for various mixtures of reactants and products, the products having been isolated by the method described below. The isosbestic point occurs at *ca.* 261 mμ.

The rate of reaction was followed by measuring the optical density at 240, 245, and 250 mμ. The absorption increases at all these wavelengths as the reaction proceeds. The kinetic experiments were carried out with at least a ten-fold excess of nitric acid, thus ensuring first-order kinetics.

The fraction (x) of reaction completed was determined at each of the three wavelengths by using the expression $x = (\varepsilon - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1)$, where ε is the apparent molar extinction coefficient of the solution at time t, ε_1 that of the starting material, and ε_2 that of the product. Values of x determined at each of the wavelengths were averaged and the mean was used in calculating the rate-constants by the usual first-order formula.

Spectrophotometric measurements were made with 1 cm. silica cells on a Unicam S.P. 500 spectrophotometer.

Typical Run.—Nitric acid (0·11 ml.) was added to a 0·0100M-solution of *m*-nitrotoluene (10 ml.) in sulphuric acid (79·9%) at 25°. Portions (1 ml.) were withdrawn at various times and quenched in water (100 ml.). The optical density (D) was measured immediately. The following results were obtained:

Time (min.)	0	0·92	1·85	2·84	4·84	6·80	8·84	∞
D	0·401	0·431	0·463	0·490	0·531	0·560	0·580	0·645
k_1 (min.$^{-1}$)	—	0·143	0·151	0·160	0·157	0·155	0·150	—

Mean $k_1 = 0{\cdot}153$ min.$^{-1}$; k_1 (graphical) $= 0{\cdot}150$ min.$^{-1}$.

The results for various sulphuric acid solutions are set out in Table 1.

Competitive Nitrations.—Overall reactivities were determined by competitive nitrations, the mixtures being analysed by gas-chromatography. The relative decreases in the amounts of the reactants after the nitration were measured.

Typical Procedure.—Nitric acid (0·004 mole) in sulphuric acid was added to one half of a mixture of the two competing substances (0·008 mole each) in 97% sulphuric acid (25 ml.) during 1 hr. with stirring. The temperature was kept at 25° ± 0·5°. After another hour

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[8] Clark and Taylor, *Org. Synth.*, 1941, Coll. Vol. I, p. 415.

[9] Page and Heasman, *J.*, 1923, **123**, 3235.

[10] Staedel, *Annalen*, 1882, **217**, 187.

[11] Cohen and McCandlish, *J.*, 1905, **87**, 1257.

[12] Brady, Day, and Rolt, *J.*, 1922, **121**, 526.

[13] Cf. Cohen and Dakin, *J.*, 1901, **79**, 1111.

[14] Deno, Peterson, and Sacher, *J. Phys. Chem.*, 1961, **65**, 199; Jones and Thorn, *Canad. J. Res.* 1949, **27**, *B*, 580.

TABLE 1.

Nitration of *m*-nitrotoluene in sulphuric acid.

H_2SO_4, % (w/w)	$-J_0$ *	[m-NO_2·C_6H_4Me] $\times 10^2$ (M)	[HNO_3] (M)	k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)
72·28	12·2	2·50	0·328	0·0004	0·0014
74·73	12·8	2·50	0·328	0·0031	0·010
76·64	13·6	2·50	0·328	0·016	0·050
78·60	13·8	1·00	0·164	0·043	0·26
79·90	14·2	1·00	0·164	0·15	0·91
81·53	14·5	0·500	0·066	0·32	4·9
84·71	15·4	0·100	0·012	0·73	60·0
87·30	16·1	0·033	0·003	1·8	~600

* These are the revised values of J_0 for pure H_2SO_4 determined by Deno and Stein [7] which they termed the C_0 function. It is here assumed that the addition of nitric acid does not appreciably alter these values.

water was added, the solution was shaken four times with ether, and the ether extracts were dried (Na_2SO_4), concentrated to small bulk, and analysed by gas-chromatography. The other half of the original mixture was similarly extracted and analysed.

Gas-chromatography.—Two columns were used. Column A (18 ft. × 0·25″) was packed with silicone fluid M.S. 550 (25% w/w) coated on Celite (80—100 mesh) and operated at 187°. Nitrogen (0·95 l./hr.) was used as carrier gas. Column B of similar dimensions was packed with 2,4,7-trinitrofluorenone (30% w/w) coated on Celite (60—80 mesh) and operated at 200°. Nitrogen (1·2 l./hr.) was here also used as the carrier gas. The retention times of the *o*-, *m*-, and *p*-nitrotoluene were 40, 47, and 51 min., respectively, on column A, and 50, 62, and 71 min., respectively, on column B. Although giving excellent resolution, column B had only a limited life at the temperature used owing to the volatility of the stationary phase,[15] and it had to be frequently renewed.

The nitrated and the unchanged extracts were injected into the column and by comparison of the areas of the peaks of the competing substances before and after nitration the amounts of each used up in the nitrations were calculated.

The accuracy of the method was checked by analysing mixtures of known composition. These mixtures were also put through the extraction procedure to ensure that no preferential loss of any component occurred. In one or two cases preferential adsorption on the drying agent was observed and so this step was omitted in subsequent experiments.

The peak areas were calculated from the triangles formed by tangents to the Gaussian curve and the interpolated base line. The relative rates were calculated from the equation [16] $k_x/k_y = \log (x/x_0)/\log (y/y_0)$, where x_0 and y_0 are the initial concentrations, and x and y are the final concentrations. The overall reactivities are set out in Table 2. In all cases the values recorded are mean values for at least four determinations analysed in duplicate. The results were reproducible within ±5%.

TABLE 2.

Relative rates of nitration of the mononitrotoluenes.

Competing substances X	Y	k_x/k_y
o-Nitrotoluene	*m*-Nitrotoluene	2·23
p-Nitrotoluene	*m*-Nitrotoluene	1·14
o-Nitrotoluene	*p*-Nitrotoluene	2·02

Product Analysis for m-*Nitrotoluene.*—*Nitration procedure.* Nitrations were carried out at 25° in 97% sulphuric acid. Nitric acid (0·06 mole) was added to a mixture of *m*-nitrotoluene (0·06 mole) in sulphuric acid (0·5 mole) during 1 hr. with stirring. The temperature was kept constant within 0·5°. The mixture was poured into water and shaken four times with ether or benzene. After being washed with sodium hydrogen carbonate and dried ($MgSO_4$) the

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[15] Cf. Norman, *Proc. Chem. Soc.*, 1958, 151.

[16] Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959; Dewar, Mole, and Warford, *J.*, 1956, 3576; Knowles and Norman, *J.*, 1961, 2938.

solvent was distilled off under reduced pressure. The residue was transferred quantitatively to a molecular still. Any unchanged *m*-nitrotoluene was removed by moderate heating at low pressure. The residual material both before and after redistillation was shown by analysis to consist entirely of dinitrotoluenes (Found: C, 46·4; H, 3·4; N, 15·6; O, 34·6. Calc. for $C_7H_6N_2O_4$: C, 46·1; H, 3·3; N, 15·4; O, 35·1%). The yield of dinitrotoluenes was usually greater than 95%.

Colorimetric determination of 3,5-*dinitrotoluene*. With alkaline acetone 3,5-dinitrotoluene gives a deep purple colour,[17] whereas the 3,4-, 2,3-, and 2,5-dinitro-isomers give red, pink, and yellow colours, respectively. Under standard conditions the purple colour is reasonably stable and gives a quantitative indication of the amount of the 3,5-dinitro-compound present. After prolonged storage the determination is affected by the red colour, which deepens with time and shifts to longer wavelengths, being due to the 3,4-dinitro-isomer (present in great excess).

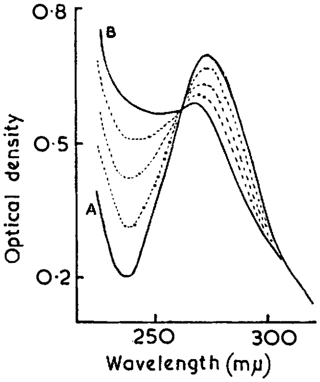

FIG. 1. Spectra of mixtures (10^{-4}M) of *m*-nitrotoluene and its nitration product in water: (A) *m*-nitrotoluene; (B) nitration product. Intermediate curves are for mixtures of (A) and (B) in the ratio 1 : 3, 1 : 1, and 3 : 1, respectively.

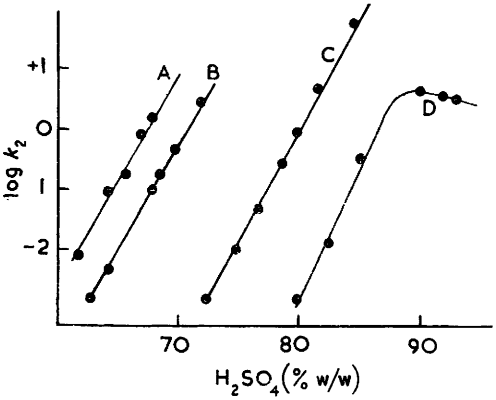

FIG. 2. Variation of log k_2 with H_2SO_4 (%): (A) benzene (ref. 7); (B) chlorobenzene (ref. 7); (C) *m*-nitrotoluene (present work); (D) nitrobenzene (ref. 5).

The standard reagent was prepared from N-sodium hydroxide (2·0 ml.) and water (20 ml.) made up to one l. with acetone.

The standard reagent (50 ml.) was added to the nitration product (0·01—0·02 g.) in acetone (5 ml.). After 5 min., the optical density at 570 mμ was rapidly measured.

A calibration curve was constructed from mixtures of known composition. The other expected isomers and *m*-nitrotoluene did not interfere under the conditions used.

The mean value obtained from quadruplicate determinations for each of five nitrations was 1·4 ± 0·1% of 3,5-dinitrotoluene.

DISCUSSION

Dependence of Rate on Acidity.—Fig. 2 is a plot of log k_2 for the nitration of *m*-nitrotoluene against percentage of sulphuric acid. Data are included for benzene,[7] chlorobenzene,[7] and nitrobenzene.[5] The values obtained for *m*-nitrotoluene coincide almost exactly with those for the trimethyl-*p*-tolylammonium ion.[18]

The rate of nitration of aromatic substrates in media containing sulphuric acid goes through a maximum, whose position depends on the particular substrate and varies over the range 89—93% sulphuric acid.[19] Possible explanations for this have recently been

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[17] Cf. Canback, *Svensk Kem. Tidskr.*, 1948, **58**, 101; English, *Analyt. Chem.*, 1948, **20**, 745.

[18] Williams and Lowen, *J.*, 1950, 3315.

[19] Cf. Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.

summarised by de la Mare and Ridd,[20] the most likely involving variation, with acidity, of both the degree of protonation of the substrate and the activities of the reactants or the transition states. The rate of nitration of *m*-nitrotoluene is too rapid for accurate measurement by conventional techniques above *ca.* 85% sulphuric acid. There was no indication of the approach of the rate maximum from the approximate value in 87% sulphuric acid and presumably this lies at slightly higher acidities out of reach of direct measurement.

If the rate of nitration follows the J_0 acidity function rather than the H_0 acidity function, we should expect the relation:

$$\log k_2 = -J_0 + \text{Constant}, \qquad (3)$$

which on differentiation with respect to the sulphuric acid concentration becomes

$$\text{d} \log k_2/\text{d}[H_2SO_4] = -\text{d}J_0/\text{d}[H_2SO_4]. \qquad (4)$$

Thus for a reaction which is more similar in type to the ionisation of an alcohol (J_0 correlation) than to protonation of a neutral substate (H_0 correlation) the rate of change of log k_2 with solvent composition should follow the rate of change of J_0 rather than of H_0 with solvent composition.

The value for *m*-nitrotoluene (d log k_2/d[H_2SO_4,%], 0·40) is in keeping with the values obtained[7] for benzene (0·21—0·36), chlorobenzene (0·23—0·35), nitrobenzene (0·39), and trimethyl-*p*-tolylammonium ion (0·40). Thus the value of log k_2 for *m*-nitrotoluene is correlated more closely, as expected, with $-\text{d}J_0/\text{d}[H_2SO_4,\%]$ (0·26), than with $-\text{d}H_0/\text{d}[H_2SO_4,\%]$ (0·13) over the range studied.

The plots of log k_2 against $-J_0$ and $-H_0$ are both linear with slopes of 1·6 and 3·0, respectively, indicating better correlation with J_0 than with H_0. The fact that the slope of the J_0 plot is considerably greater than unity shows that the reaction is subject to a fairly strong salt effect, which superposes itself on the expected rate-dependence, as occurs with bromination by hypobromous acid.[21] Distinction between the two possible brominating agents Br^+ and $BrOH_2^+$ can, in principle, be made. The slopes of the J_0 and H_0 plots for bromination are, however, respectively, less and greater than unity, which makes clear distinction difficult. This illustrates the need for further determinations of the J_0 function under conditions of constant ionic strength.

Overall Reactivity.—The relative rates of nitration of the mononitrotoluenes in 97% sulphuric acid (Table 2) are $k_o : k_m : k_p = 2{\cdot}23 : 1{\cdot}00 : 1{\cdot}14$, in good agreement with those for 82·5% sulphuric acid determined approximately by Westheimer and Kharasch,[5] *viz.*, 2·3 : 1·0 : 1·2. The effect of changing the composition of the solvent on the rate of nitration of aromatic substrates varies considerably from one compound to another.[19,20,22] In the present case, however, there is probably some variation since the comparison is over rather a wide range of solvent composition and it is possible that the good agreement between the two sets of results is, in part, fortuitous.

From Fig. 2 the rate constants for the nitration of *m*-nitrotoluene and nitrobenzene in 84% sulphuric acid are found to be 31·6 and 0·078 l. mole^{-1} min.$^{-1}$, respectively, *i.e.*, the relative rates are in the ratio 395 : 1. If it is assumed that this ratio does not vary greatly with increase in sulphuric acid concentration, then by combining this ratio with the relative rates for *m*- and *p*-nitrotoluene in 97% sulphuric acid ($k_m : k_p = 1{\cdot}00 : 1{\cdot}14$), *p*-nitrotoluene is calculated to undergo nitration *ca.* 430 times faster than nitrobenzene. Considering the nature of the assumption involved this is in not too great a disagreement

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[20] de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publns., London 1958, 63.

[21] de la Mare and Hilton, *J.*, 1962, 997.

[22] Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955.

with the experiments of Brand and Paton[23] which indicate that, for nitration in 99% sulphuric acid, the rate factor is *ca.* 330.

In Fig. 2 the rate constants for nitration of benzene and chlorobenzene in 68% sulphuric acid are seen to be 1·56 and 0·102 l. mole^{-1} min.$^{-1}$, respectively. Also, in 72% sulphuric acid the rate constants for the nitration of chlorobenzene and *m*-nitrotoluene are 2·82 and 0·0010 l. mole^{-1} min.$^{-1}$, respectively. The relative rates in the two cases are, therefore, 15·3 : 1, and 2820 : 1. If it is assumed that the plots of log k_2 against percentage of sulphuric acid for all of these compounds remain parallel throughout the range of acid concentration under consideration (68—84%), then by a stepwise procedure it is calculated that the rates of nitration of benzene and nitrobenzene are in the ratio $1 : 6 \times 10^{-8}$. This accords reasonably with the experiments of Westheimer and Kharasch[5] who showed that the introduction of another nitro-group into *p*-nitrotoluene reduces the rate of nitration by a factor of *ca.* 10^7.

Orientation and Partial Rate Factors.—By combining the relative rate of nitration of nitrobenzene and the proportion of products obtained[24] (*ortho* 6·8%, *meta* 91·8%, *para* 1·4%), the following partial rate factors for nitrobenzene can be calculated: f_o, $1{\cdot}22 \times 10^{-8}$; f_m, $16{\cdot}5 \times 10^{-8}$; f_p, $0{\cdot}5 \times 10^{-8}$. The partial rate factors recorded for the nitration of toluene[25] and t-butylbenzene,[26] together with those calculated for nitrobenzene, allow estimates to be made of the relative reactivities of the various positions in the nitrotoluenes and in the nitro-t-butylbenzenes, additivity being assumed for the effects of the substituents on the free energies of activation for substitution at the various positions.[27] The results are approximations since the various nitrations were carried out under different conditions. The predicted orientations are set out in Table 3.

The predictions for the expected orientation of products from *o*- and *p*-nitrotoluene are in reasonable qualitative accord with observation. Thus *o*-nitrotoluene[4] gives only the 2,4- (66·6%) and 2,6- (33·3%) dinitro-products: Kobe and his co-workers, using the isotope dilution technique, have shown[28] that $\ngtr$0·4% of 2,3-dinitro-isomer can be present. *p*-Nitrotoluene yields exclusively the 2,4-dinitro-product[4] and $\ngtr$0·2% of the 3,4-dinitro-isomer can be present.[29]

TABLE 3.

Predicted orientations for nitration.

	Product (%)					
Substrate	2,3-	2,4-	2,5-	2,6-	3,4-	3,5-
o-Nitrotoluene	1·82	57·8	0·07	41·9	—	—
m-Nitrotoluene	27·6	—	11·6	—	38·2	22·6
p-Nitrotoluene	—	99·7	—	—	0·3	—
m-Nitro-t-butylbenzene	4·0	—	1·6	—	54·4	40·0

The predictions for *m*-nitrotoluene are, however, considerably at variance with the observed isomer distribution. One would expect that the 3,5-dinitro-product should constitute some 22% of the product. The actual amount formed was 1·4%. The predictions for the 2,3- and 3,4-dinitro-isomers are only in fair agreement with the observed products (25% and 55%, respectively). The predicted percentage of the 2,5-nitro-compound is, however, considerably below that obtained.

p-Nitro-t-butylbenzene gives exclusively the 2,4-dinitro-product,[23] in agreement with the predicted orientation (not shown here). The predictions for *m*-nitro-t-butylbenzene

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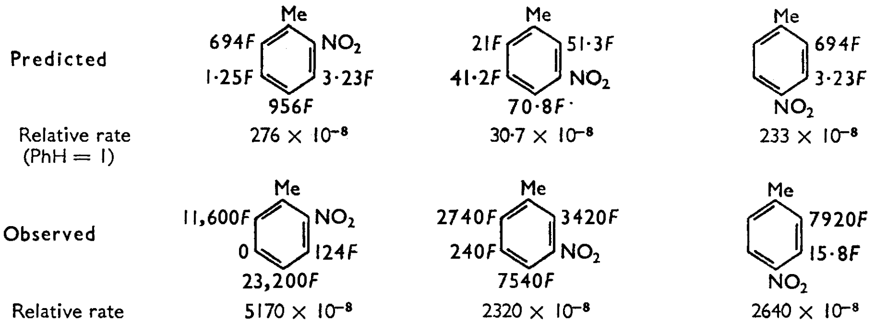
[23] Brand and Paton, *J.*, 1952, 281.
[24] Holleman, *Chem. Rev.*, 1925, **1**, 187.
[25] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.
[26] Nelson and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 5605.
[27] Bradfield and Jones, *Trans. Faraday Soc.*, 1941, **37**, 726.
[28] Roberts, Browder, and Kobe, *J. Amer. Chem. Soc.*, 1959, **81**, 1165.
[29] Roberts, Watkins, and Kobe, *J. Amer. Chem. Soc.*, 1959, **81**, 1167.

are much less accurate than for *m*-nitrotoluene. Ayad and Garwood [2] found that the product of nitration consisted almost entirely of 3,4-dinitro-t-butylbenzene with small amounts of the 3,5-dinitro-compound: they were unable to identify either the 2,3- or the 3,6-dinitro-isomer. Theoretical predictions indicate that the product should consist of mainly the 3,5- (54·5%) and 3,5-dinitro-compound (40·0%), with *ca.* 4% and 1·6%, respectively, of the 2,3- and 3,6-dinitro-isomer.

The worst discrepancies between observation and theory seem to arise for the *m*-nitroalkylbenzenes. The same kind of discrepancy has been noted in the prediction of orientation for the nitration of the chlorotoluenes and it has been suggested [30a] that in these cases the additivity principle underestimates the rate of substitution in positions that are strongly deactivated by one substituent but are less deactivated, or are activated, by the other. This can be seen more clearly by considering the partial rate factors for the various positions in the mononitrotoluenes. The values obtained are set out below, where the factor F (10^{-8}) is included to make the actual quantities less unwieldy.



The partial rate factors have been calculated from the relative rates and the observed isomer distributions. The proportions of 2,3-, 2,5-, and 3,4-dinitrotoluene found [4] in the nitration of *m*-nitrotoluene have been modified to allow for the presence of 1·4% of the 3,5-dinitro-isomer which was found in the present investigation, the whole set of values being normalised to 100%.

The partial rate factors for the 3-position in *o*- and *p*-nitrotoluene are based on the maximum figures quoted by Kobe and his co-workers [28,29] (see above). Therefore these partial rate factors have to be regarded as being only very approximate. The value of zero for the 5-position in *o*-nitrotoluene has to be regarded similarly, since the presence of only 0·1% of the 2,5-dinitro-isomer would lead to a significant value for the partial rate factor because the relative rate is so much greater than could be predicted.

With the possible exception of position 5 in *o*-nitrotoluene, all the positions in the three mononitrotoluenes are more reactive than would be predicted from the additivity principle, by a factor which seems to be greater for positions *ortho* and *para* than for positions *meta* to a nitro-group. Breakdown of the additivity principle might be expected in disubstituted benzenes where the two substituents are *para* to each other, as in *p*-nitrotoluene, and where conjugation can modify the reactivity of the various positions.[30b] It is not immediately apparent, however, why all the mononitrotoluenes should have such a high overall reactivity.

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[30] Ref. 20, (*a*) p. 90, (*b*) p. 91.