The Duality of Mechanism for Nitration in Acetic Anhydride

By J. G. HOGGETT, R. B. MOODIE, and K. SCHOFIELD*
(*Department of Chemistry, University of Exeter, Stocker Road, Exeter*)

SOLUTIONS of acetyl nitrate in acetic anhydride (formed by the addition of nitric acid to acetic anhydride) have been much used in studying aromatic nitration. The nature of the effective nitrating agent in these solutions is disputed, the claims of protonated acetyl nitrate,[1,2] nitronium ion,[3] and dinitrogen pentoxide[4,5] having been urged. The situation has been excellently reviewed.[3] We show that at least two mechanisms of nitration can operate; and shall later argue for the specific identification of the reagents involved.

The nitration of benzene and some more reactive compounds by solutions of acetyl nitrate in acetic anhydride at 25° has been studied. The nitrating solutions were prepared from *pure* nitric acid and pure acetic anhydride. The rates of nitration of mesitylene, *o*-xylene, *m*-xylene, and anisole were independent of the concentration and nature of the aromatic compound (as shown by earlier workers for the xylenes[2]) provided that $[\mathrm{ArH}] \nless ca.\ 10^{-1}\,\mathrm{M}$; in agreement with other workers[2] we found the reactions of *m*-xylene and *o*-xylene to be complicated by the occurrence of acetoxylation, and for these compounds the sums of the rates of acetoxylation and nitration are considered. No products of acetoxylation were found in the nitration of mesitylene or anisole. The concentration of aromatic needed to maintain zeroth order kinetics is much greater than for nitration with solutions of nitric acid in sulpholan,[6] and modification of the reaction to one kinetically of the first order in the concentration of the aromatic was obtained when $[\mathrm{ArH}] < ca.\ 2 \times 10^{-2}\,\mathrm{M}$.

Under these first order conditions the rates of nitration of a number of compounds in acetic anhydride have been determined, the nitrating solution having been prepared with an initial concentration of pure nitric acid of 4×10^{-2} — 3·0 M (see Table). The data show that a limit to the rate of reaction is reached at about 10^3 times the rate for benzene. This limit, which we take to be the rate of encounter between the aromatic and the nitrating agent, is somewhat higher than has been observed in other media.[6,7]

Under the same conditions of reaction anthanthrene, diphenylamine, phenol, and resorcinol were nitrated seven to ten times faster than mesitylene. The reactions of these compounds were not always kinetically of the first order in the concentration of the aromatic, and those of phenol and resorcinol were prone to autocatalysis. These observations relate to solutions prepared from *pure* nitric acid where $[HNO_2] < ca. 10^{-4}$ M. If the nitrating solutions were kept for several hours before use (when nitrous acid is developed[8]), or if "fuming" nitric acid were used in their preparation, the rates of nitration of these four compounds were enormously accelerated. This phenomenon is also shown by most of the compounds which react at the limiting rate when pure nitric acid is used.

The behaviour of the very reactive substrates mentioned strongly suggests that nitration *via* nitrosation is accompanying another process of nitration (associated with a limiting encounter rate), but the possibility is not absolutely excluded of the occurrence of nitration by an electrophile much less reactive than that involved in the latter process. Whichever explanation is correct, it is clear that there is at least a dichotomy in the mechanism of nitration for very reactive compounds, and that, unless the contributions of the separate mechanisms can be distinguished, quantitative comparisons of reactivity are meaningless.

It is opportune to report here another observation relevant to the present problem. The supposed change in the orientation of nitration of anisole when reaction occurs in acetic anhydride[9,10] as compared with reaction in sulphuric acid[10] has commonly been regarded as evidence for a change in mechanism.[11] We find that anisole is nitrated in acetic anhydride at the limiting rate to give 70% of *o*- and 30% of *p*-nitroanisole, in agreement with previous work.[9,10] However, when anisole was nitrated at the encounter rate in 65% aqueous sulphuric acid, and under zeroth order conditions with nitric acid in sulpholan the proportions were 60% and 40%, and 70% and 30% of *o*- and *p*-nitroanisole, respectively. In both of these latter conditions [where urea (*ca.* 10^{-2} M) was present] nitration involves the nitronium ion. When anisole was nitrated in 65% sulphuric acid in the absence of urea and in the presence of added sodium nitrite (*ca.* 4×10^{-2} M) the proportion of isomers changed dramatically to 94% of *p*- and 6% of *o*-nitroanisole. Thus, the earlier results did contain an anomaly but it resided in the results for nitration in sulphuric acid; we suggest that in the earlier work[10] some of the nitration in sulphuric acid proceeded *via* nitrosation.

Nitration in acetic anhydride at 25°

Compound	Relative rate[a]
Mesitylene	1·0
Anisole	0·74
m-Dimethoxybenzene	0·64
1-Methylnaphthalene	0·25
1,6-Dimethylnaphthalene	0·50
Naphthalene	0·076
o-Xylene	0·12
m-Xylene	0·21
Pyrene	0·79
Thiophen	0·36
Toluene[b]	0·009—0·013

[a] Rates relative to that for mesitylene at the same concentration of nitric acid for each substrate. The relative rates for toluene and benzene were 37 : 1 ($[HNO_3] = 1·3$ M).

[b] The uncertainty in this value arises from the need to extrapolate the plot of $\log_{10}k$ v $\log [HNO_3]$ to obtain overlap between that for mesitylene and that for toluene.

(*Received, April 9th,* 1969; *Com.* 482.)

---

[1] F. G. Bordwell and E. W. Garbisch, *J. Amer. Chem. Soc.*, 1960, **82**, 3588.
[2] A. Fischer, A. J. Read, and J. Vaughan, *J. Chem. Soc.*, 1964, 3691.
[3] J. H. Ridd in "Studies on Chemical Structure and Reactivity," Methuen, London, 1966.
[4] V. Gold, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1950, 2467.
[5] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 1961, 3030.
[6] J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1969, 1.
[7] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.
[8] F. H. Cohen and J. P. Wibaut, *Rec. Trav. Chim.*, 1935, **54**, 409.
[9] K. Halvarson and L. Melander, *Arkiv Kemi*, 1957, **11**, 77.
[10] P. H. Griffiths, W. A. Walkey, and H. B. Watson, *J. Chem. Soc.*, 1934, 631. C. A. Bunton, G. J. Minkoff, and R. I. Reed, *J. Chem. Soc.*, 1947, 1416.
[11] P. B. D. de la Mare and J. M. Ridd, "Aromatic Substitution: Nitration and Halogenation," Butterworth, London, 1959, p. 76.