The Encounter Rate in Aromatic Nitration in Sulphuric Acid

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THE rate of nitration of benzene by solutions of nitric acid in 51—68% sulphuric acid has been reported by Deno and Stein[1] and it is believed that the nitronium ion is the effective electrophile in this medium. Comparison of the calculated[2] rate coefficient ($\sim 10^9$ l. mole^{-1} sec.$^{-1}$) of encounter between the nitronium ion and the substrate, and the observed rate coefficient of nitration indicates that, if allowance is made for the low concentration of nitronium ion, the observed rate is fairly close to the expected limit represented by the encounter rate.[3]

Since Deno and Stein's work has been used as a basis for the calculation of partial rate factors[2,4,5] the possibility that diffusion is the rate-controlling process assumes great importance.

To clarify this point and to determine the magnitude of the limiting rate controlled by diffusion, the rates of nitration of benzene, toluene, *o*-, *m*-, and *p*-xylene, and mesitylene by solutions of nitric acid in 68·3% sulphuric acid at 25° have been determined. The results of this work are shown in the Table, which also includes the slopes $[-\mathrm{d}(\log_{10}k_2)/\mathrm{d}(H_\mathrm{R} + \log_{10} a_{\mathrm{H_2O}})]$ of the rate profiles of some of these substrates at this acidity, where H_R stands for the acidity function controlling the ionisation in sulphuric acid of triarylcarbinols. The possibility of nitration *via* nitrosation was eliminated by a study of the effect of the presence of urea on these nitrations.

The limiting encounter rate of nitration for substituted benzenes seems to be approximately forty times the rate of nitration of benzene at this acidity. Further examples of substrates which are nitrated at the encounter rate are naphthalene and 2-methylnaphthalene (see Table). The observations[1,6] that both anisole and *m*-dimethoxybenzene are nitrated at a rate about fifty times that of benzene in 63% sulphuric acid, add further experimental support for the hypothesis of rate control by encounter.

The simplest assumption to be made from the observation that the difference between the reactivity of toluene and benzene is close to that observed in less viscous systems[7] is that the rate of nitration of benzene is not affected by diffusion control. The above results therefore indicate that partial rate factors for substrates, less reactive than benzene in nitration by nitronium ion formed *in situ* from nitric acid, are meaningful and can be used as measures of aromatic reactivity, but that such comparisons lose their meaning for activated substrates.

To provide a solid basis for comparison the rate of nitration of benzene is being studied over a wide range of acidity and the value[5] of $[-\mathrm{d}(\log_{10}k_2)/$

TABLE

Rate of nitration of reactive substrates by nitric acid in 68·3% *sulphuric acid at* 25°

Substrate	k_2 (l. mole^{-1}sec.$^{-1}$)*	$\frac{-\mathrm{d}(\log_{10}k_2)}{\mathrm{d}(H_R + \log_{10} a_{H_2O})}$†
Benzene	0·058	0·99
Toluene	1·0	0·97
p-Xylene	2·2	—
o-Xylene	2·2	—
m-Xylene	2·2	—
Mesitylene	2·1	0·85
Naphthalene	1·5	1·0
2-Methylnaphthalene ..	1·5	—

* Second-order rate coefficient referred to nitric acid concn.
† At this acidity.

$\mathrm{d}(H_R + \log_{10} a_{H_2O})$] has been found to be significantly greater than unity at higher acidities. This will affect previously calculated partial rate factors to a small extent.

The reported high selectivity for nitration of highly activated substrates such as mesitylene, naphthalene derivatives, and polynuclear aromatic hydrocarbons[8] in organic solvents seems to indicate, even when the lower viscosities of these solvents are taken into consideration, that the nitronium ion is not the effective electrophile in these specific cases, and that reaction either occurs by another nitrating electrophile or *via* nitrosation. It is not yet possible to add to the general conclusions drawn[7] as to the role of the nitronium ion in these solvents. However, we are attempting to extend to such systems the criterion of the encounter rate.

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