

A Simple Linear Description of Rate Profiles for the Nitration of Aromatic Compounds in the Critical Range 80—98 wt% Sulphuric Acid

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A new treatment shows a linear relationship between the M_C activity coefficient function and rate profiles for aromatic compounds whose nitration occurs in concentrated sulphuric acid.

Rate profiles for aromatic compounds whose nitration occurs in concentrated sulphuric acid (80—98 wt %) show a maximum

at *ca.* 90 wt % from the values of the second-order rate constants¹ {see Figure 1(a) where $[A_R]_{st}$ and $[HNO_3]_{st}$ are

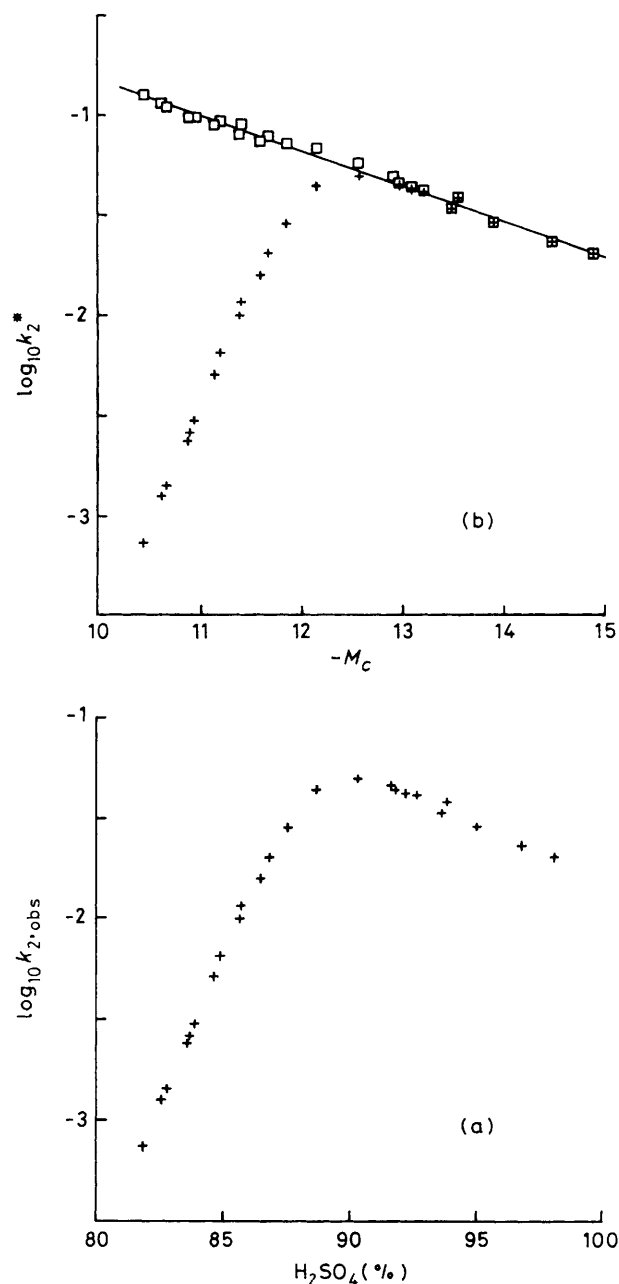


Figure 1. Rate profiles for nitration in 80–98 wt% H_2SO_4 of nitrobenzene at 25 °C using $[\text{A}_\text{R}]_\text{st} = 10^{-4} \text{ mol dm}^{-3}$ and $[\text{HNO}_3]_\text{st} = 10^{-1}–10^{-2} \text{ mol dm}^{-3}$. (a) Values of $\log k_{2,\text{obs}}$ vs. wt% H_2SO_4 ($k_{2,\text{obs}}$ in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). (b) (+) Values of $\log k_{2,\text{obs}}$ vs. M_c ; (□) values of $\log k_2^*$ vs. M_c (see text).

the initial concentrations of aromatic compound, A_R , and nitric acid, respectively}. The occurrence of this maximum is still not well understood, notwithstanding the recognition of different empirical explanations.^{1–4} Moreover, this behaviour may be a complication in the study of the relative reactivities of deactivated substrates and/or recognition of the reacting species (AR or ARH^+).¹

We therefore suggest a new treatment of experimental data based on the nature of the solute species and on M_c activity coefficient function^{5–7} at different acid concentrations.

Accurate concentration values of NO_3^- , HNO_3 , and NO_2^+ species at 25 °C are now available,^{8,9a} from careful Raman and u.v. measurements of the equilibria of nitric acid in water–sulphuric acid solutions (range 0–98 wt% H_2SO_4). For the aromatic solutes (A_R and $\text{A}_\text{R}\text{H}^+$), the corresponding protonation equilibrium has to be considered in the studied acidity range.

To illustrate the proposed procedure we report in Figure 1(b) the observed rate constants $\{\log k_{2,\text{obs}} = \log [\text{rate}/([\text{A}_\text{R}]_\text{st}[\text{HNO}_3]_\text{st})]\}$ of nitrobenzene, obtained at 25 °C in the range 80–98 wt% sulphuric acid.^{9a} The nitrobenzene is nitrated as free base. Indeed, u.v. studies in H_2SO_4 and H_2SO_4 – SO_3 solutions⁹ show the nitro-group of nitrobenzene not to be appreciably protonated in the range where the nitration rates are measured.

The same Figure 1(b) shows the linear profile obtained by plotting vs. M_c the logarithm of the observed rate constant (k_2^*) corrected for the actual concentration of the NO_2^+ nitrating agent, i.e. $k_2^* = k_{2,\text{obs}}[\text{HNO}_3]_\text{st}/[\text{NO}_2^+]$ where $[\text{HNO}_3]_\text{st} = [\text{HNO}_3] + [\text{NO}_3^-] + [\text{NO}_2^+]$. Therefore, the resulting linear relationship may be represented by equation (1)

$$\text{Rate} = K_2^\circ [\text{A}_\text{R}] [\text{NO}_2^+] 10^{nM_\text{c}} \quad (1)$$

where K_2° and n are the relevant thermodynamic parameters.

It should be noted that the use of the M_c activity function allows account to be taken of the actual rather than stoichiometric concentrations. Preliminary results confirm the validity of equation (1) for all tested aromatic compounds.

The proposed procedure gives a simple linear description of the nitration rates in concentrated acid solutions allowing the entire rate profiles to be determined from the knowledge of the two relevant parameters. Thus rate constants can be predicted over the whole range from a few measurements. Moreover, it can remove the difficulties¹⁰ related to the utilization of the $\log k_{2,\text{obs}}$ plots vs. sulphuric acid percentage. Indeed, the use of the latter simple data treatment applied in the high acidity range does not allow a simple interpretation of rate maximum to be made.

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