Thermodynamic Nitration Rates of Aromatic Compounds. Part 2.† Linear Description of Rate Profiles for the Nitration of Aromatic Compounds in the Range 40—98 wt% Sulphuric Acid ‡

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New studies of nitration in sulphuric acid have been made at high acidities (80—98 wt% H_2SO_4) where at 90 wt% a maximum occurs in the observed rate constant for aromatic compounds. A new treatment of experimental data is reported which takes into account the effective concentration of solutes and changes in the $f_{Ar}f_{NO_2^+}/f^\ddagger$ ratio with acidity, using the M_C function. Compounds nitrating at low and high acidity are tested, and representative examples of the results obtained are given. Experimental evidence points to two significant findings in this study. The variation in the observed rate constants below and above 90 wt% H_2SO_4 is related to ionization of nitric acid to give NO_2^+ ions. The new procedure applied to the kinetic data allows us to obtain a linear description of rate profiles for substrates reacting as free bases in the range 40—98 wt% H_2SO_4.

The nitration of aromatic compounds in dilute or concentrated aqueous sulphuric acid has long been known to exhibit second-order kinetics.[1,2] The observed rates are related to the stoicheiometric concentrations of reacting compounds by equation (1). The behaviour of the rate constants *versus* the

$$\text{Rate} = k_{2\text{obs.}}\,[\text{ArH}]_{\text{st}}\,[\text{HNO}_3]_{\text{st}} \qquad (1)$$

medium composition, however, shows a different trend below and above 90% sulphuric acid.[1,2] A steep increase up to a maximum is observed in going from dilute solutions to 90% acid. Conversely a gentle decrease is found in 90—98% H_2SO_4 where the nitric acid is completely converted into NO_2^+.[1-4] In the whole acidity range the nitronium ion is recognized as the nitrating agent[1,2] and its concentration does not decrease as the acid percentage increases.[4,5] Different explanations[1,2,6-9] have been advanced for the unexpected rate decrease.

To gain insight into the problem, all the solutes involved in the reaction are taken into account and the variation of reaction rates with the acidity of the medium is analysed by the M_C activity coefficient function.[10-12] Such a description is a continuation of earlier studies[13] restricted to compounds whose nitration occurs up to 88 wt% H_2SO_4 and such a study is a part of a continuing effort to develop reliable treatments to describing the behaviour of nitrating acid solutions.

According to transition state theory, the rate of unprotonated or protonated substrates reacting through the Wheland intermediate in the rate-determining step can be set in form (2)[14] where $[\text{ArH}]_{\text{st}}$ stands for [ArH] or $[\text{ArH}_2^+]$ and $f^\ddagger$ is the

$$\text{Rate} = k_2^\circ\,[\text{ArH}]_{\text{st}}[\text{NO}_2^+]\frac{f_{\text{ArH}}\,f_{\text{NO2}^+}}{f^\ddagger} \qquad (2)$$

activity coefficient of the transition state. From (1) and (2), equation (3) is obtained .

$$k_{2\text{obs.}}\,[\text{ArH}]_{\text{st}}[\text{HNO}_3]_{\text{st}} = k_2^\circ\,[\text{ArH}]_{\text{st}}[\text{NO}_2^+]\frac{f_{\text{ArH}}\,f_{\text{NO2}^+}}{f^\ddagger} \qquad (3)$$

The above equation can be tested in the range of sulphuric acid where the nitration is observed (*ca.* 40—98 wt% H_2SO_4), provided $[NO_{2+}]$ and $f_{\text{ArH}}\,f_{NO_2^+}/f^\ddagger$ can be estimated.

To estimated NO_2^+, the equilibria (4) and (5) of nitric acid

$$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^- \qquad (4)$$

$$\text{HNO}_3 + \text{H}^+ \rightleftharpoons \text{NO}_2^+ + \text{H}_2\text{O} \qquad (5)$$

have been studied in different water–sulphuric acid mixtures (*ca.* 1—98 wt% H_2SO_4) by Raman and u.v. measurements.[4,5] The corresponding equilibrium constants can be written as (6) and (7). The knowledge of the activity coefficient term is of

$$K_{\text{HNO}_3} = \frac{[\text{NO}_3^-][\text{H}^+]}{[\text{HNO}_3]}\cdot\frac{f_{\text{NO}_3-}f_{\text{H}^+}}{f_{\text{HNO}_3}} \qquad (6)$$

$$K_{\text{NO}_2^+} = \frac{[\text{HNO}_3][\text{H}^+]}{[\text{NO}_2^+]\text{a}_{\text{w}}}\cdot\frac{f_{\text{HNO}_3}f_{\text{H}^+}}{f_{\text{NO}_2^+}} \qquad (7)$$

importance in this chemical system since we are concerned with weak bases in concentrated acid solutions. Then, in agreement with previous work[10-12] we assume that the M_C activity coefficient ratio of solutes, *i.e.* equation (8), holds

$$M_{\text{C}} = -\log_{10}\frac{f_{\text{B}_i}f_{\text{A}_i}}{f_{\text{C}_i}} = -n_{ij}\log_{10}\frac{f_{\text{B}_j}f_{\text{A}_j}}{f_{\text{C}_j}} \qquad (8)$$

where B = base, A = acid, and C = conjugated acid.

The validity of relationship (8) has been widely tested, in protonation and ionization equilibria.[11,12] Concentration values obtained by using equation (8) are in very good agreement with experimental results.[11,12] This suggests that the concentration of NO_2^+, as well as that of solutes involved in equilibria (6) and (7), can be evaluated with some confidence in the whole acidity range from: $\text{p}K_{\text{HNO}_3} \cong -2.25$; $\log_{10}(f_{\text{NO}_3-}\,f_{\text{H}+}/f_{\text{HNO}_3}) \cong 0.338\,M_{\text{C}}$ and $\text{p}K_{\text{NO}_2^+} \cong -16.05$; $\log_{10}(f_{\text{HNO}_3}f_{\text{H}^+}/f_{\text{NO}_2^+}] \cong 0.98\,M_{\text{C}}$. The M_C values are taken from ref. 12.

Furthermore, we assume that the M_C function is able to describe the activity coefficient ratio of the nitration rate process[14,15] [see equation (2)]. Then, equation (3) can be rewritten as (3′). From (3′), equations (9) and (10) have been

$$k_{2\text{obs.}}\,[\text{ArH}]_{\text{st}}[\text{HNO}_3]_{\text{st}} = k_2^\circ\,[\text{ArH}]_{\text{st}}[\text{NO}_2^+]\,10^{nM_{\text{C}}} \qquad (3')$$

derived and used for analysing the kinetic data, where $f_{\text{ArH}}f_{\text{NO}_2^+}/f^\ddagger = 10^{nM_{\text{C}}}$; $f_{\text{ArH}}f_{\text{NO}_2^+}f_{\text{HNO}_3}f_{\text{H}^+}/f^\ddagger f_{\text{NO}_2^+} = 10^{n'M_{\text{C}}}$; and $n' = n + 0.98$.

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† Part 1 is ref. 13.

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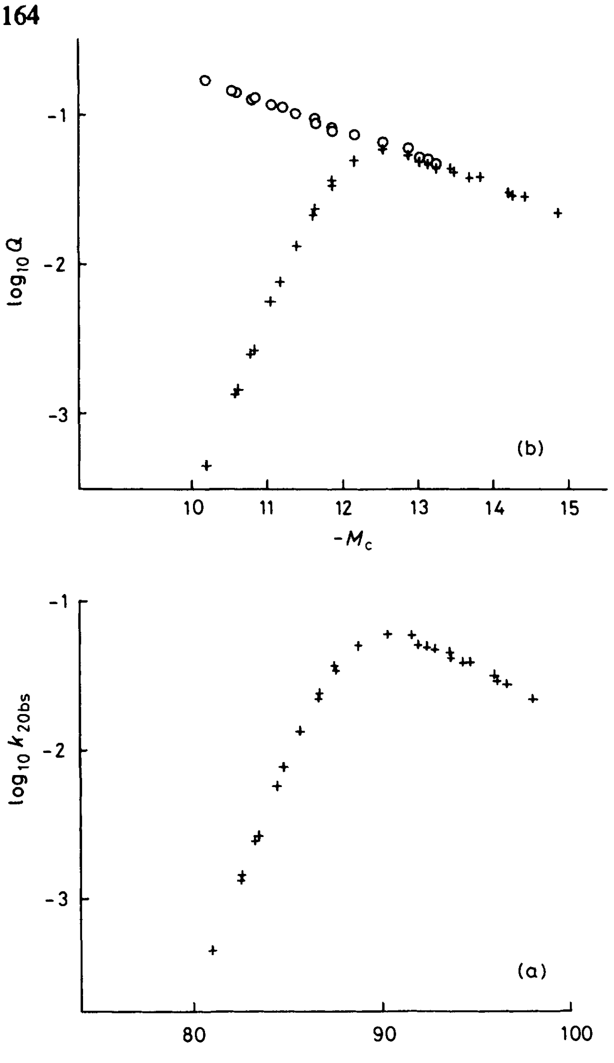

Figure 1. Rate profiles for the nitration in 80—98 wt% H_2SO_4 of methyl phenyl sulphone at 25 °C. (a) Values of $\log_{10} k_{2\mathrm{obs.}}$ *versus* tw% H_2SO_4 (see Table 1); (b) + values of $\log_{10} k_{2\mathrm{obs.}}$ *versus* M_C; o values of $\log_{10}$ Q *versus* M_C (see text)

$$k_{2\mathrm{obs.}}\left\{1+\frac{[\mathrm{NO_3^-}]}{[\mathrm{HNO_3}]}+\frac{[\mathrm{NO_2^+}]}{[\mathrm{HNO_3}]}\right\}\frac{[\mathrm{HNO_3}]}{[\mathrm{NO_2^+}]}=k_2^\circ\,10^{nM_\mathrm{C}} \qquad (9)$$

$$k_{2\mathrm{obs.}}\left\{1+\frac{[\mathrm{NO_3^-}]}{[\mathrm{HNO_3}]}+\frac{[\mathrm{NO_2^+}]}{[\mathrm{HNO_3}]}\right\}\frac{a_\mathrm{w}}{[\mathrm{H^+}]}=\frac{k_2^\circ}{K_{\mathrm{NO_2^+}}}\,10^{n'M_\mathrm{C}} \qquad (10)$$

This procedure has been applied to the nitration of nitrobenzene and methyl phenyl sulphone in the range 80—98 wt% H_2SO_4. The experimental $k_{2\mathrm{obs.}}$ which have been used are in the Table. In the high acidity range investigated, these substrates undergo nitration as unprotonated species, according to Raman and u.v. studies in H_2SO_4–H_2O and H_2SO_4–SO_3.[5,16,17]

Indeed, literature data for nitrobenzene,[16,17] and new experimental results[5] for both compounds, show that their protonation occurs above 99 wt% sulphuric acid.

Preliminary results of the new procedure using nitrobenzene as reacting compound have already been published.[18] The behaviour of methyl phenyl sulphone is shown in Figure 1 where the rate profile obtained by plotting log $k_{2\mathrm{obs.}}$ *versus* the percentage of sulphuric acid is compared with that obtained by plotting $\log_{10} Q$ *versus* M_C where Q is the left-hand side of equation (9). The very good linear relationship observed for the above substrates supports the validity of the new treatment.

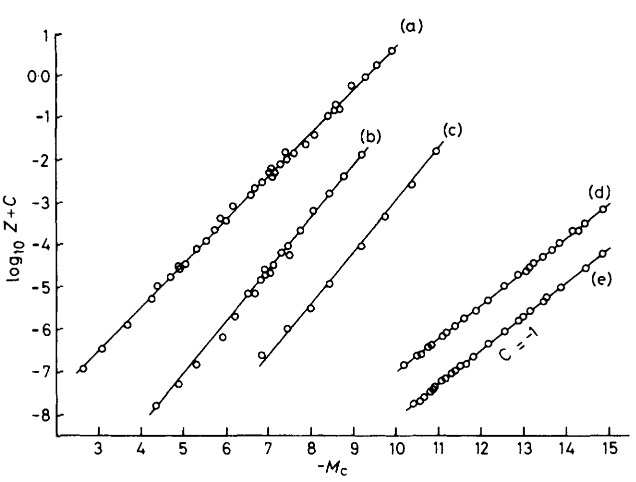

Figure 2. Nitration in 40—98 wt% H_2SO_4 of (a) anisole, (b) fluorobenzene, (c) *p*-dibromobenzene; (d) methyl phenyl sulphone; (e) nitrobenzene. Values of $\log_{10} Z$ *versus* M_C (see text). Experimental data of (a) from refs. 25—27; (b) from refs. 25, 28, 29; (c) from ref. 30; (d) and (e) in the Table. Except for (e), the constant *c* is zero

A linear relationship can also be obtained by plotting $\log_{10} Z$ *versus* M_C where Z is the left-hand side of equation (10). Obviously, the difference between the two intercepts referred to aqueous standard state gives the $\mathrm{p}K_{\mathrm{NO_2^+}}$ value of equilibrium (5).

In Figure 2 the plots of $\log_{10} Z$ *versus* M_C are reported for some aromatic compounds being nitrated in the range 40—98 wt% H_2SO_4. The linear rate profiles observed at low and high acidity show that the new treatment is a suitable description of the entire nitration rate behaviour. Alternatively the good description of the rate process over a wide acidity range strongly supports the validity of the M_C method.

The results for nitrobenzene and methyl phenyl sulphone allow an interpretation of the variation of the observed rate profiles in the range 80—98 wt% H_2SO_4. This behaviour has to be expected since it is related below 90 wt% H_2SO_4 to variation of the NO_2^+/HNO_3 ratio while above 90 wt% H_2SO_4 the concentration of the nitrating agent is constant and the right-hand side of equation (9) reproduces the observed rate decrease (see Figure 1).

Taking equation (2) into account the decrease in rate above 90 wt% H_2SO_4 is related to the decrease of activity coefficient ratio, as NO_2^+ is constant in this range. This behaviour could be mainly due to the f_{ArH} decrease which has been measured for some aromatic compounds.[14,19,20] However, on the basis of our treatment, we cannot estimate the extent of the variation of a particular activity coefficient.

Further comment would require the description of the equilibrium (5) whose ionization, like that of triarylcarbinols, is usually given by equation (7).[14] Indeed this equation can be written as (11)[21] and instead of equation (8) we could assume a slightly different definition for the M_C function, *i.e.* equation

$$K_{\mathrm{NO_2^+}}=\frac{[\mathrm{HNO_3}][\mathrm{H^+}]}{[\mathrm{NO_2^+}][\mathrm{H_2O}]}\cdot\frac{f_{\mathrm{HNO_3}}f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}f_{\mathrm{H_2O}}} \qquad (11)$$

$$M_\mathrm{C}=-n\log_{10}\left\{\frac{[\text{Product of activity coefficient of reactants}]}{[\text{Product of activity coefficient of products}]}\right\} \qquad (12)$$

Table. Second-order rate coefficients (k_2/dm^3 mol^{-1} s^{-1}) for nitration in aqueous sulphuric acid at 25 ± 0.1 °C

Nitrobenzene [a]

H_2SO_4 (wt%)	$\log_{10} k_{2obs.}$ [b]	H_2SO_4 (wt%)	$\log_{10} k_{2obs.}$ [b]
81.81	−3.135	86.30	−1.800
81.81	−3.115	86.74	−1.690
82.42	−2.950	87.45	−1.545
82.53	−2.905	88.81	−1.360
82.74	−2.850	90.27	−1.305
83.36	−2.650	91.53	−1.335
83.36	−2.620	91.72	−1.360
83.61	−2.585	91.72	−1.355
83.73	−2.525	91.94	−1.375
84.40	−2.995	92.18	−1.385
84.56	−2.270	92.44	−1.380
84.84	−2.185	93.58	−1.470
84.84	−2.215	93.78	−1.420
85.42	−2.000	93.78	−1.420
85.42	−2.005	94.96	−1.535
85.66	−1.935	96.76	−1.631
86.29	−1.780	96.76	−1.635
86.30	−1.790	98.01	−1.690

Methyl phenyl sulphone [a]

H_2SO_4 (wt%)	$\log_{10} k_{2obs.}$ [b]	H_2SO_4 (wt%)	$\log_{10} k_{2obs.}$ [b]
80.89	−3.345	90.27	−1.225
82.42	−2.860	91.53	−1.260
82.49	−2.845	92.03	−1.310
83.33	−2.595	92.39	−1.320
83.39	−2.590	92.76	−1.330
84.41	−2.245	93.57	−1.385
84.80	−2.120	93.58	−1.365
85.66	−1.875	94.29	−1.435
86.69	−1.640	94.76	−1.425
86.74	−1.630	95.98	−1.515
87.60	−1.445	96.12	−1.550
87.60	−1.465	96.65	−1.560
88.81	−1.305	98.01	−1.660

[a] [Aromatic] 10^{-4}—10^{-5} mol dm^{-3}, [HNO_3] 10^{-2}—10^{-1} mol dm^{-3}.
[b] Estimated percentage of standard error 2.5—3.0%.

(12) where *n* depends on a particular equilibrium. Equation (12) relates the M_C value to the ratio of activity coefficients of all species involved in an equilibrium reaction. This suggests that M_C could describe the dissociation of the acid itself within the solution. If so, the M_C description of equilibria would be free from the formal species which effectively enter into the process as it occurs in dilute solution.

Unfortunately, preliminary trials were found not to descriminate between equations (8) and (12) owing to experimental errors. Further tests are in progress.

Experimental

Second-order rate constants for the nitration of nitrobenzene and methyl phenyl sulphone at 25 °C have been given previously.[22,23] New kinetic runs are now reported using a sophisticated experimental technique in order to minimize random as well as systematic errors.

Materials.—Purified aromatic compounds checked by g.l.c. or t.l.c. have been used. Nitric acid vacuum distilled from concentrated sulphuric acid (1 : 2 v/v) was used and stored at −50 °C. Sulphuric acid was AnalaR grade and the percentage composition of solutions was determined by automatic potentiometric titrations against standard solutions of sodium hydroxide. Titrations were performed on an Amel 234 instrument, using a digital burette. Each percentage value was the average of at least ten measurements and the estimated error was *ca.* 0.1%. Two different normal solutions of HCl were used for the standardization of normal solutions of NaOH. The sample were always weighed or drawn off by a Chemetron micrometric syringe with the greatest possible accuracy.

Kinetic Measurements.—Separate solutions of aromatic compounds and nitric acid in the appropriate concentration of sulphuric acid were prepared using weighed samples either of reagents or of solvent. Samples of sulphuric–nitric mixtures were weighed in a u.v. silica cell and thermostatted at 25 °C. A small volume of a thermostatted solution of aromatic compound was added at the start. The concentrations of the reagents were calculated by measuring the solution densities, using a precision micrometric syringe. The changes of absorbance over time, at selected wavelengths, were recorded by a Perkin-Elmer 554 spectrophotometer equipped with a thermostatted thermoelectric cell holder and a digital controller. The kinetic runs were performed in sulphuric acid solutions after titration. By using nitric acid concentrations of *ca.* 10^{-1}—10^{-2}M, at least ten times those of the substrates (*ca.* 10^{-4}—10^{-5}M), good linear pseudo-first-order kinetic plots were obtained. The $k_{2obs.}$ values were calculated from the stoicheiometric concentrations of nitric acid. Second-order rate constants for the nitration at 25 °C of the substrates are given in the Table. Taking experimental error into account, the new rate values are in agreement with the literature results.[22,23] The products of nitrobenzene nitrated in different sulphuric acid concentrations were also tested and analysed by g.l.c. The isomeric distribution does not change with acidity, in agreement with literature results.[24]

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