Thermodynamic Nitration Rates of Aromatic Compounds. Part 1. The Nitration of Benzene and Some Benzene Derivatives in Aqueous Sulphuric and Perchloric Acids. A Comparison of the Results referred to Water as Standard State

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Thermodynamic nitration rates, k_2^0, referred to water as standard state, are recorded for some aromatic compounds which are nitrated *via* Wheland intermediates. The values have been calculated by a new mechanistic criterion involving the M_C activity coefficient relationship, and using experimental rate constants, $k_{2,obs.}$, measured both in sulphuric and perchloric acid. The validity of the results and the confidence intervals of the values are discussed. A new nitration scale of reactivity, relative to benzene, is given for some substituted benzene derivatives. Discussions on the rate-determining step of benzene are also reported, accounting for the results in the range 51—82% H_2SO_4 and 57—65% $HClO_4$

THE nitration of aromatic compounds in aqueous sulphuric and perchloric acids can be studied successfully on the basis of M_C activity coefficient functions.[1-5] This new procedure appears to be of considerable interest in the analysis of kinetic data, as a source of information either for mechanisms of reactions or for parameters having a thermodynamic bearing. Here, we present the first results of such a study, applied to benzene and to some monosubstituted benzene derivatives. The validity and the significance of the new procedure are also discussed, since this provides a different viewpoint for assessing relative rates from that previously determined using observed rate constants.

Thermodynamic nitration rates of aromatic compounds which are nitrated through Wheland intermediates can be obtained by equation (1), accounting for the dissociation of nitric acid to give NO_2^+ ions[5,6] [equilibrium (2)].

$$\log k_2^0 = \log k_{2,\mathrm{obs.}} - \log[\mathrm{H}^+] + \log a_\mathrm{w} - \log K_{\mathrm{HNO_3}} - \log\frac{f_{\mathrm{Ar}}f_{\mathrm{NO_2^+}}}{f^\ddagger} - \log\frac{f_{\mathrm{HNO_3}}f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} \quad (1)$$

$$\mathrm{HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-} \quad (2)$$

Equation (1) is applicable to unprotonated (free bases) or protonated substrates (conjugate acids), undergoing nitration in *ca.* $50\mathrm{wt}\% < H_2SO_4 < 88\mathrm{wt}\%$ and *ca.* $50\mathrm{wt}\% < HClO_4 < 72\mathrm{wt}\%$ acidity ranges. The reaction model (1), for each aromatic compound, can be experimentally verified by (3), using plots of log V_i (where $\log V_i = \log k_{2,\mathrm{obs.}} - \log[\mathrm{H}^+] + \log a_\mathrm{w}$) against the M_C function.

$$\log k_{2,\mathrm{obs.}} - \log[\mathrm{H}^+] + \log a_\mathrm{w} = -(n_{\mathrm{Ar}} + n_{\mathrm{HNO_3}})M_\mathrm{C} + (\log k_2^0 - \mathrm{p}K_{\mathrm{HNO_3}}) \quad (3)$$

The possibility of rewriting equation (1) as (3) derives from the validity, previously tested,[4,5,7,8] of relationships (4) and (5). It follows that linear correlations are expected for nitration occurring *via* a σ complex as the rate-determining step.

Examples of particular interest for determining the validity of the new treatment are in Tables 1A and 2 since these sections are concerned with substrates whose nitration has been studied in aqueous sulphuric and perchloric acid, using large acidity ranges. These

$$-\log\frac{f_{\mathrm{Ar}}f_{\mathrm{NO_2^+}}}{f^\ddagger} = n_{\mathrm{AR}}M_\mathrm{C} \quad (4)$$

$$-\log\frac{f_{\mathrm{HNO_3}}f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} = n_{\mathrm{HNO_3}}M_\mathrm{C} \quad (5)$$

substrates are also of special value because their isomeric compositions and reacting species are independent of any variation of acidity.[9-11]

In considering the results, several data support the validity of equation (3).† The most obvious piece of evidence in sulphuric acid derives mainly from the linearity of the plots of log V_i *versus* M_C (Figure 1). This linearity is observed over a wide acidity range and for all available experimental data (Table 1A). Further, the results in perchloric acid, where the general pattern of the plots is similar to that observed in sulphuric acid, are in agreement with equation (3). The log V_i values, in perchloric acid, are calculated by using both the rate coefficients in the literature and the new ones listed in the Experimental section. The evidence, which is highly significant, comes from a comparison of the intercepts obtained in sulphuric and perchloric acid. The same values are obtained, within experimental error, for analogous compounds in different acids (Table 3). This guarantees confidence in the validity of the new procedure. The accuracy of the numerical values is assured by using a revised M_C scale.[8]

The above arguments all suggest that benzene and halogenobenzenes react by a nitration mechanism according to equation (1). With benzene, however, a different reaction path was suggested as a result of studies using the H_R acidity function.[6] In particular, the curvature observed for the plots log $k_{2,\mathrm{obs.}}$ *versus* H_R and *versus* $(H_R + \log a_\mathrm{w})$[6,11,12] suggested a change of

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† The validity of equation (3) comes from the circumstance that the relation $\log V_i = n^*M_\mathrm{C} + \text{constant}$ is experimentally verified, so that the relations: $n^* = n_{\mathrm{Ar}} + n_{\mathrm{HNO_3}}$ and constant $= \log k_2^0 - \mathrm{p}K_{\mathrm{HNO_3}}$ can be written.

TABLE 1

Nitration in aqueous sulphuric acid at 25 °C. Parameters of plots of log $V_{\text{corr.}}$ * *versus* M_C according to equation (3)

Compound	Range % H_2SO_4	Slope † $= (n_{AR} + n_{HNO_3})$	Intercept ‡ $= \log k_2^0 - pk_{HNO_3}$	σ_y §	r ¶	No. of points	Ref.
1A							
Benzene	51.1—69.1	−1.365 ± 0.080	−13.081 ± 0.185	0.034	0.9979	9	*a*
	63.2—82.2	−1.266 ± 0.031	−12.152 ± 0.123	0.015	0.9988	19	*b, c*
	62.4—71.8	−1.340 ± 0.031	−12.744 ± 0.101	0.015	0.9987	23	*d*
	51.1—82.2	−1.341 ± 0.024	−12.794 ± 0.085	0.012	0.9981	51	*a—d*
Fluorobenzene	54.0—70.0	−1.312 ± 0.082	−13.590 ± 0.206	0.035	0.9976	9	*a*
	67.5—77.0	−1.256 ± 0.044	−12.992 ± 0.134	0.017	0.9995	7	*e*
	65.8—69.9	−1.269 ± 0.027	−13.122 ± 0.057	0.008	0.9999	5	*d*
	54.0—77.0	−1.349 ± 0.042	−13.741 ± 0.137	0.020	0.9979	21	*a, d, e*
Chlorobenzene	57.0—72.0	−1.373 ± 0.068	−14.339 ± 0.175	0.028	0.9988	8	*a*
	67.5—77.4	−1.274 ± 0.026	−13.404 ± 0.080	0.010	0.9998	7	*e*
	65.8—73.4	−1.344 ± 0.030	−13.913 ± 0.076	0.011	0.9999	6	*d*
	57.0—77.4	−1.388 ± 0.052	−14.329 ± 0.175	0.025	0.9970	21	*a, d, e*
Bromobenzene	57.0—72.0	−1.356 ± 0.059	−14.257 ± 0.153	0.024	0.9990	8	*a*
	67.5—74.7	−1.372 ± 0.105	−14.160 ± 0.178	0.024	0.9997	4	*e*
	65.8—73.4	−1.399 ± 0.124	−14.378 ± 0.318	0.045	0.9980	6	*d*
	57.0—74.7	−1.417 ± 0.056	−14.560 ± 0.179	0.026	0.9973	18	*a, d, e*
Iodobenzene	67.5—74.9	−1.225 ± 0.108	−12.581 ± 0.190	0.025	0.9996	4	*e*
	65.8—73.4	−1.184 ± 0.062	−12.283 ± 0.158	0.022	0.9993	6	*d*
	65.8—74.9	−1.203 ± 0.034	−12.410 ± 0.108	0.015	0.9994	10	*d, e*
p-Dichlorobenzene	73.2—87.7	−1.279 ± 0.059	−15.510 ± 0.256	0.026	0.9981	11	*e*
1B							
$Ph[CH_2]_3\overset{+}{N}Me_3$	61.0—68.3	−1.299 ± 0.360	−12.112 ± 0.170	0.028	0.9998	3	*f*
$Ph[CH_2]_2\overset{+}{N}Me_3$	63.4—76.5	−1.218 ± 0.168	−12.689 ± 0.288	0.039	0.9990	4	*f*
$PhCH_2\overset{+}{N}Me_3$	74.5—81.6	−1.066 ± 0.109	−14.854 ± 0.364	0.039	0.9973	6	*f, g*
$Ph\overset{+}{N}Me_3$	82.0—87.5	−0.975 ± 0.038	−17.283 ± 0.186	0.017	0.9987	11	*h, i*
	82.0—86.0	−1.020 ± 0.045	−17.752 ± 0.178	0.016	0.9995	6	*h, i*
PhCN	80.0—85.0	−1.098 ± 0.120	−18.029 ± 0.472	0.046	0.9956	7	*a*

* By using rate constants corrected in the range < 73% H_2SO_4 for lowering of HNO_3 concentration due to the ionization $HNO_3 \rightleftharpoons H^+ + NO_3^-$. The value −2.529, obtained by Raman spectroscopy (unpublished results), was used. † Slope ± 95% confidence limit. ‡ Intercept ± standard error. § σ_y is the standard deviation of points from the linear regression line in the y direction. ¶ Correlation coefficient.

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TABLE 2

Nitration in aqueous perchloric acid at 25 °C. Parameters of the plots of log V *versus* M_C according to equation (3)

Compound	Range % $HClO_4$	Slope † $= (n_{Ar} + n_{HNO_3})$	Intercept ‡ $= \log k_2^0 - pk_{HNO_3}$	σ_y §	r ¶	No. of points	Ref.
Benzene	57.1—64.4	−1.503 ± 0.061	−13.194 ± 0.146	0.022	0.9996	6	*a*
	58.0—64.0	−1.446 ± 0.042	−12.934 ± 0.121	0.018	0.9994	10	*b*
	57.1—64.4	−1.473 ± 0.072	−13.069 ± 0.225	0.034	0.9963	16	*a, b*
Fluorobenzene	60.4—68.0	−1.420 ± 0.240	−13.484 ± 0.415	0.056	0.9984	4	*c*
	59.6—66.5	−1.520 ± 0.042	−14.134 ± 0.131	0.018	0.9995	9	*b*
	59.6 68.0	−1.470 ± 0.064	−13.793 ± 0.214	0.029	0.9978	13	*c, b*
Chlorobenzene	60.4 68.0	−1.448 ± 0.189	−14.063 ± 0.327	0.044	0.9991	4	*c*
	60.8 67.1	−1.503 ± 0.046	−14.367 ± 0.134	0.018	0.9996	7	*b*
	60.4—68.0	−1.478 ± 0.067	−14.220 ± 0.223	0.030	0.9982	11	*c, b*
Bromobenzene	61.1—66.5	−1.493 ± 0.084	−14.336 ± 0.049	0.006	0.9999	3	*c*
	60.8—67.1	−1.503 ± 0.024	−14.407 ± 0.073	0.009	0.9999	7	*b*
	60.8—67.1	−1.500 ± 0.017	−14.387 ± 0.051	0.007	0.9999	10	*c, b*
Iodobenzene	61.1—66.5	−1.282 ± 1.094	−12.339 ± 0.638	0.086	0.9977	3	*c*
	61.6—66.2	−1.358 ± 0.171	−12.943 ± 0.400	0.054	0.9977	5	*b*
	61.1—66.5	−1.317 ± 0.102	−12.625 ± 0.310	0.042	0.9970	8	*c, b*
p-Dichlorobenzene	64.4—71.8	−1.317 ± 0.070	−14.579 ± 0.222	0.025	0.9992	6	*d*

†—¶ See Table 1.

[a] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800. [b] Present work. [c] R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1970, 347. [d] R. B. Moodie, K. Schofield, and P. N. Thomas, *J.C.S. Perkin II*, 1978, 318.

Table 3

Thermodynamic rate constants (log k_2^0) and thermodynamic reaction rates, relative to benzene (log Z_r^0), referred to water as standard state, for nitration of some aromatic compounds at 25 °C

Compound	Intercept [a] in H_2SO_4	Intercept [a] in $HClO_4$	Intercept [b] (average)	log k_2^0 [c] (Thermodynamic)	log Z_r^0 (Thermodynamic)	log Z_r' (observed) [d] % H_2SO_4	log Z_r' (observed) [d] % $HClO_4$
Benzene	−12.794	−13.069	−12.931	2.047	0.000	0.000	
Fluorobenzene	−13.741	−13.793	−13.767	1.212	−0.835	−0.683 (54.0) −0.909 (77.0)	−0.715 (59.6) −0.651 (64.0)
Chlorobenzene	−14.329	−14.220	−14.274	0.704	−1.343	−1.175 (57.0) −1.179 (77.4)	−1.158 (60.4) −0.995 (64.0)
Bromobenzene	−14.560	−14.387	−14.473	0.505	−1.542	−1.175 (57.0) −1.179 (74.7)	−1.049 (60.8) −1.051 (64.0)
Iodobenzene	−12.410	−12.625	−12.518	2.461	+0.413	−0.435 (65.8) −0.795 (74.9)	−0.626 (61.7) −0.677 (64.0)
p-Dichlorobenzene	−15.510	−14.579	−15.045	−0.0658	−2.113	−3.240 (73.2) −3.308 (82.2)	−2.712 (64.4)
$Ph[CH_2]_3\overset{+}{N}M_3$	−12.112			+2.867	+0.819	+0.601 (61.0) +0.356 (68.3)	
$Ph[CH_2]_2\overset{+}{N}Me_3$	−12.689			+2.289	+0.242	−0.593 (63.4) −1.035 (76.5)	
$PhCH_2\overset{+}{N}Me_3$	−14.854			+0.125	−1.922	−4.392 (74.5) −4.808 (81.6)	
$Ph\overset{+}{N}Me_3$	−17.752			−2.774	−4.821	−8.184 (82.0)	
PhCN	−18.029			−3.050	−5.098	−7.444 (80.0) −7.711 (82.0)	

[a] Values obtained using all the available experimental points. [b] Average of the values in sulphuric and perchloric acids. [c] log k_2^0 = intercept − pK_{HNO_3} (pk_{HNO_3} = −14.979 obtained by Raman spectroscopy).[5] The average of the intercepts, obtained from sulphuric and perchloric acids, has been used when available. [d] Observed rates of nitration, relative to benzene, at given acidities, (percentages of acids at the end of experimental points available have been chosen).

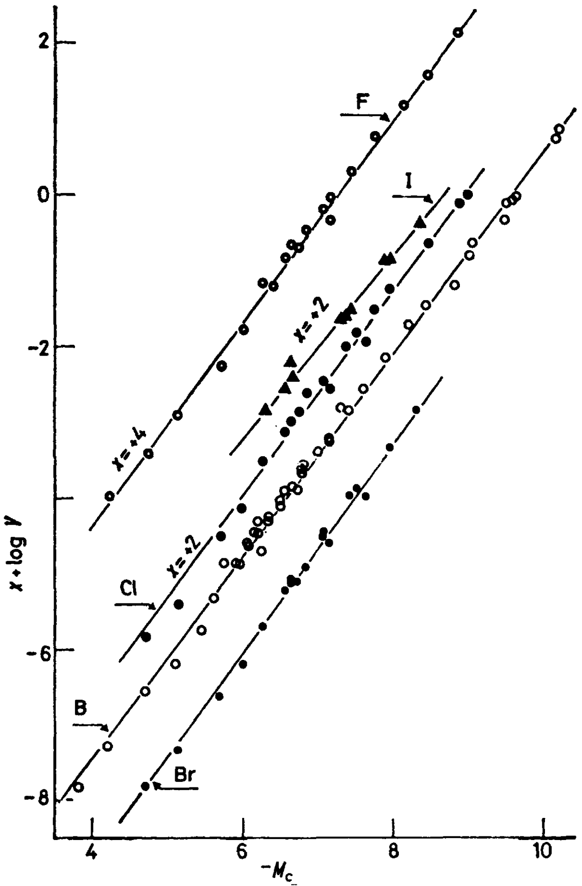

Figure 1 Plots of (x + log V) against $-M_C$, (log V = log $k_{2,obs.}$ − log $[H^+]$ + log a_w) for the nitration at 25 °C in aqueous sulphuric acid of fluorobenzene (F), iodobenzene (I), chlorobenzene (Cl), benzene (B), bromobenzene (Br). Experimental data in Table 1; M_C values from ref. 8

nitration mechanism above 68% sulphuric acid[6,12-16] and a limited encounter reaction was postulated.[6,12] Further, the linearity observed for the plots log $k_{2,obs.}$ *versus* H_0,[11,17] in the range 51—82% H_2SO_4, * is difficult to fit in with the previous interpretations.

In distinguishing amongst the different patterns for benzene, it is useful to establish the validity of the criteria on the basis of which the various alternatives have been postulated. The breakdown of the acidity functions[2,3] suggests that any use of them generally give too coarse results to be useful in discriminating amongst different mechanistic paths. The nitration of halogenobenzenes, analysed in terms of H_0, H_R, and (H_R + log a_w) functions, supports analogous conclusions.[4,11] M_C Functions, on the contrary, do not have the limitations of acidity functions.[1-3,8,18] It follows that analysis by log V_i *versus* M_C plots should give a satisfactory test of benzene nitration.

Further, the possible involvement of an encounter reaction for benzene has been tested. It was made by comparing the second-order rate coefficients for the reaction between benzene and nitronium ions (k_2') † with those expected from diffusion theory ($k_{2,enc.}$) ‡ [Figure 2(a)]. Reliable k_2' values are utilized here for the comparison, since in evaluating them, precise data for $[HNO_3]/[NO_2^+]$, as obtained by Raman spectroscopy,[5] were used.

On the basis of the new results, the nitration rate of benzene differs from the limiting encounter rate at least by a factor of *ca.* 200 (at 80% of H_2SO_4). Moreover, as

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* The linear dependence of the rates on H_0 reported in ref. 17 concerns only the range 63—71% H_2SO_4.

† Where $k_2' = k_{2,obs.}[HNO_3]/[NO_2^+]$ using $[HNO_3]/[NO_2^+]$ values obtained by Raman spectroscopy.[5]

‡ Calculated from the equation[19] $k_{2,enc.} = 8\,RT/3\mu$.

shown in Figure 2(b), log $k_{2,\mathrm{enc.}}$ is linearly related to log k_2' in the whole acidity range. Similar trends, incompatible with the encounter of reactants in a rate-determining step, are observed for deactivated compounds, *e.g.* for bromobenzene [Figure 2(b)].

The following discussion involves an extension of the M_C approach applied to all compounds in Tables 1 and 2. The evidence for nitration occurring *via* a Wheland intermediate allowed the calculation of thermodynamic values (k_2^0) referred to water as standard state. These values have been calculated from the intercepts in sulphuric and perchloric acid (log k_2^0 — p$K_{\mathrm{HNO_3}}$) [of equation (3)], since p$K_{\mathrm{HNO_3}}$ is known.

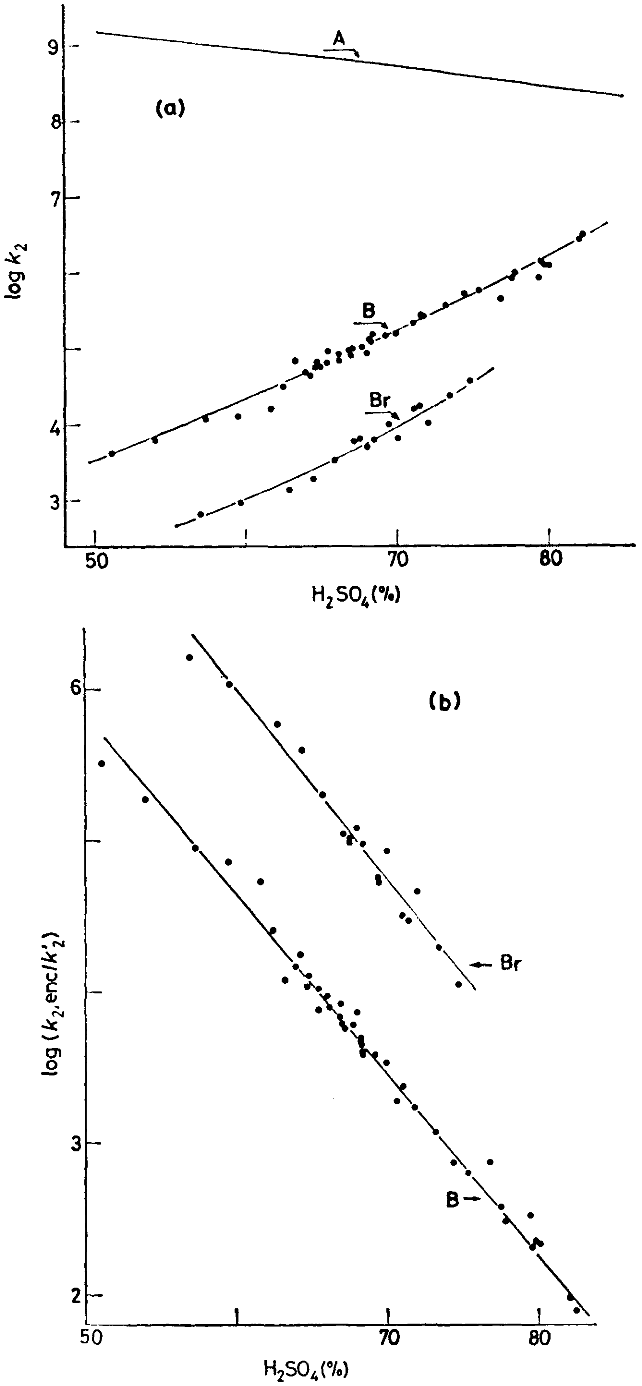

FIGURE 2 (a) Plots of log k_2 against percentage of sulphuric acid at 25 °C: log $k_{2,\mathrm{enc}}$ (A); log k_2' for the nitration of benzene (B); log k_2' for the nitration of bromobenzene (Br). (b) Plots of log $k_{2,\mathrm{enc}}/k'_2$ against percentage of sulphuric acid at 25 °C for the nitration of benzene (B) and bromobenzene (Br). (log $k_{2,\mathrm{enc}}$, log k'_2 see text)

Rates relative to benzene, using thermodynamic data (Z^0_{ri}), have also been obtained and examples of the nitration of some deactivated substrates are shown in Table 3. The results are compared with literature values calculated at a given acidity. Since the present study set out to discuss the validity of the new treatment, it appeared of interest to consider the reliability of the new reactivity scale; likewise similarities and divergences of the new values were compared with previous ones.

TABLE 4

Second-order rate coefficients (k_2/dm^3 mol^{-1} s^{-1}) for nitration in aqueous perchloric acid at 25.0 ± 0.1 °C

Compound	$HClO_4$ (%) [a]	[HNO_3]/M	log $k_{2,\mathrm{obs}}$ [c]
Benzene [b]	58.00	3.68×10^{-2}	−2.549
	58.93	2.62×10^{-2}	−2.127
	59.63	7.70×10^{-3}	−1.817
	59.63	2.57×10^{-2}	−1.792
	60.58	1.11×10^{-2}	−1.448
	61.05	1.83×10^{-2}	−1.231
	61.66	1.74×10^{-2}	−0.932
	62.14	9.61×10^{-3}	−0.707
	63.03	3.85×10^{-3}	−0.234
	63.98	4.00×10^{-3}	+0.224
Fluorobenzene [b]	59.63	7.70×10^{-3}	−2.595
	60.90	1.83×10^{-2}	−2.033
	62.02	9.77×10^{-3}	−1.399
	62.02	9.77×10^{-3}	−1.424
	63.03	3.86×10^{-3}	−0.895
	63.98	4.00×10^{-3}	−0.427
	65.56	3.33×10^{-3}	+0.450
	65.56	5.00×10^{-3}	+0.435
	66.53	8.80×10^{-4}	+0.962
Chlorobenzene	60.84	1.16×10^{-2}	−2.369
	61.78	7.53×10^{-2}	−1.857
	62.43	6.19×10^{-2}	−1.622
	64.01	5.45×10^{-3}	−0.770
	65.14	3.64×10^{-3}	−0.181
	66.18	1.51×10^{-3}	+0.435
	67.05	1.09×10^{-3}	+0.937
Bromobenzene [b]	60.84	1.79×10^{-1}	−2.379
	61.78	7.53×10^{-2}	−1.940
	62.43	6.19×10^{-2}	−1.645
	64.01	5.33×10^{-3}	−0.826
	65.14	3.64×10^{-3}	−0.186
	66.18	2.47×10^{-3}	+0.384
	67.05	1.09×10^{-3}	+0.902
Iodobenzene	61.66	1.42×10^{-2}	−1.496
	62.17	1.77×10^{-2}	−1.314
	64.01	3.63×10^{-3}	−0 453
	65.14	3.64×10^{-3}	+0.060
	66.18	2.47×10^{-3}	+0.733

[a] ±0.1%. [b] [Aromatic] = 10^{-4}—10^{-5}. [c] Estimated percentage of standard error of the mean ±2.5%.

Concerning the first question, the following two factors are significant. First, the observed linear dependence of the plots, based on a mechanistic criterion which does not involve any simplifying assumptions, and secondly, the correspondence of k_2^0 values in sulphuric and perchloric acids. These reasons suggest that confidence can be placed in the M_C treatment and numerical values. The remaining uncertainties in the k_2^0 values, accounting for the confidence intervals in the M_C functions, are mainly to be related to the errors of experimental data. The above arguments, therefore, all suggest that few experimental data over a narrow acidity range can often be misleading, while a rigorous test will provide comparisons of many nitration rate constants in different strong acids. Examples of both cases are given in Tables 1 and 2.

The opportunity of evaluating the confidence intervals also arises, since experimental data of nitrations in strong acids are available at high acidity ranges (H_2SO_4, $HClO_4 > 50$wt%) and large extrapolations are always required.

The analysis of the second question requires a comparison of $Z^0_{r_i}$ (thermodynamic relative rates) and Z'_{r_i} values (observed relative rates at given acidities) which are related by equation (6) where n_i and n_B are the slopes

$$Z^0_{r_i} = Z'_{r_i} + (n_B - n_i)M_C \qquad (6)$$

of plots of log V_i *versus* M_C for the substrate i and benzene, respectively. It can be seen that $Z^0_{r_i} \equiv Z'_{r_i}$ if $n_i \equiv n_B$. As soon as $n_i \neq n_B$, $(Z^0_{r_i} - Z'_{r_i})$ becomes a function of acidity. Small differences amongst n_i and n_B values do not necessarily give small differences amongst Z_r' and Z_r° values because of the term $(n_B - n_i)M_C$. Using the same experimental data, these reasons justify the differences between the thermodynamic and literature data in the extension which depends on the differences in n_i, n_B, and M_C values.

Subsequent papers will deal with relative substituent effects obtained from thermodynamic data.

EXPERIMENTAL

The procedure for the kinetic studies in perchloric acid closely follows that described previously for nitrations in sulphuric acid.[11] The same applies to details of purification of materials, standardization of perchloric acid, and techniques of measuring rates. The second-order rate constants for nitration at 25 °C in perchloric acid are listed in Table 4. In the range 59—68% $HClO_4$, the isomeric composition of halogenobenzenes is as observed in sulphuric acid.[11]

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