The M_C Activity Coefficient Function for Acid–Base Equilibria. Part 4.† Limitations of Empirical Relationships involving Observed Nitration Rates and Acidity Functions

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The empirical linear relationships, for moderately concentrated aqueous sulphuric acid solutions, between the observed nitration rates of aromatic compounds and the H_0, H_R, and (H_R + log a_w) functions, are discussed. In particular, their utilization as a criterion of mechanism is investigated. The rate profiles of nitration of halogenobenzenes, for which wide acidity ranges are experimentally available, are used in the analysis. The results obtained show the breakdown of previous relationships because of either their incompatibility with the mechanism of nitration (H_0 function) or the approximation intrinsic in H_R acidity function. The latter, however, should be consistent with the nitration model, providing slopes of unity are rigorously observed. A new experimental linear relationship, consistent with nitration through NO_2^+ ions, *via* a Wheland intermediate, has been found. The extension of the M_C activity coefficient treatment to acid–base equilibria involved in the nitration is presented.

NITRATION in moderately concentrated aqueous sulphuric acid is widely used for investigating substituent effects and for mechanistic criteria in different aromatic substrates.[1-3] Since rates of nitration are sensitive to medium acidity, plots relating the observed rate constants with the H_0, H_R, and (H_R + log a_w) functions, have been recognized to be a useful procedure.[1,2,4-6] In these cases, good straight lines were observed, so that the empirical correlations (1)—(3) appeared to be simultaneously verified. However, in discussing a valid criterion for the choice of relationships (1), (2), or (3), it seems useful to analyse in detail their meaning in relation to the mechanism of nitration.

$$\log k_{2(\mathrm{obs})} = -nH_0 + C \qquad (1)$$

$$\log k_{2(\mathrm{obs})} = -n'H_R + C' \qquad (2)$$

$$\log k_{2(\mathrm{obs})} = -n''(H_R + \log a_w) + C'' \qquad (3)$$

Equations (4) and (5) represent the well known mechanism for nitration of aromatic compounds (AR) *via* a Wheland intermediate, in moderately concentrated aqueous sulphuric acid solutions. The equations account for the dissociative equilibrium of non-hydrated or monohydrated nitric acid,[1,6] to give NO_2^+ ions.

$$\log k_{2(\mathrm{obs})} = \log[\mathrm{H^+}] - \log a_w + \log k_2^\circ K_{\mathrm{HNO_3}} + \log \frac{f_{\mathrm{AR}} f_{\mathrm{NO_2^+}}}{f^\ddagger} + \log \frac{f_{\mathrm{HNO_3}} f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} \qquad (4)$$

$$\log k_{2(\mathrm{obs})} = \log[\mathrm{H^+}] - 2\log a_w + \log k_2^\circ K_{\mathrm{HNO_3}} + \log \frac{f_{\mathrm{AR}} f_{\mathrm{NO_2^+}}}{f^\ddagger} + \log \frac{f_{\mathrm{HNO_3,H_2O}} f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} \qquad (5)$$

Combination of (4) with (1), by using the H_0 acidity function, leads to equation (6). Also combination of (4) with (2) and of (5) with (3), by using the H_R acidity function, gives equations (7) and (8) respectively.

$$\log \frac{f_{\mathrm{AR}} f_{\mathrm{NO_2^+}}}{f^\ddagger} + \log \frac{f_{\mathrm{HNO_3}} f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} - \log \frac{f_{\mathrm{B}} f_{\mathrm{H^+}}}{f_{\mathrm{BH^+}}} = (1 - n)H_0 + \log a_w + m \qquad (6)$$

$$\log \frac{f_{\mathrm{AR}} f_{\mathrm{NO_2^+}}}{f^\ddagger} + \log \frac{f_{\mathrm{HNO_3}} f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} - \log \frac{f_{\mathrm{ROH}} f_{\mathrm{H}}^{+}}{f_{\mathrm{R^+}}} = (1 - n')H_R + m' \qquad (7)$$

$$\log \frac{f_{\mathrm{AR}} f_{\mathrm{NO_2^+}}}{f^\ddagger} + \log \frac{f_{\mathrm{HNO_3,H_2O}} f_{\mathrm{H^+}}}{f_{\mathrm{NO_2^+}}} - \log \frac{f_{\mathrm{ROH}} f_{\mathrm{H^+}}}{f_{\mathrm{R^+}}} = (1 - n'')(H_R + \log a_w) + m'' \qquad (8)$$

These equations represent three different acidity dependencies of the rates of nitration, so that it is important to make a choice from among these alternatives. The nitration of halogenobenzenes over a wide acidity range (54—77% sulphuric acid) has been re-investigated.[7] The choice of halogenobenzenes derives from the chemical observation that they are free from any significant variation in mechanism, side reaction, or interaction with solvent, over the whole acidity range examined.[8]

The results, reported in Figure 1, show the breakdown of relationships (2) and (3) [plots of log $k_{2(\mathrm{obs})}$ *versus* H_R[9,10] (Figure 1a) and (H_R + log a_w) (Figure 1b)] as soon as wide acidity ranges are examined. The observed linear dependence (Figure 1c) of the rates on the H_0[11] acidity function is, nevertheless, unexpected because of evidence which supports the involvement of nitronium ion, rather than nitroacidium ion, in the nitration reactions.[12-14]

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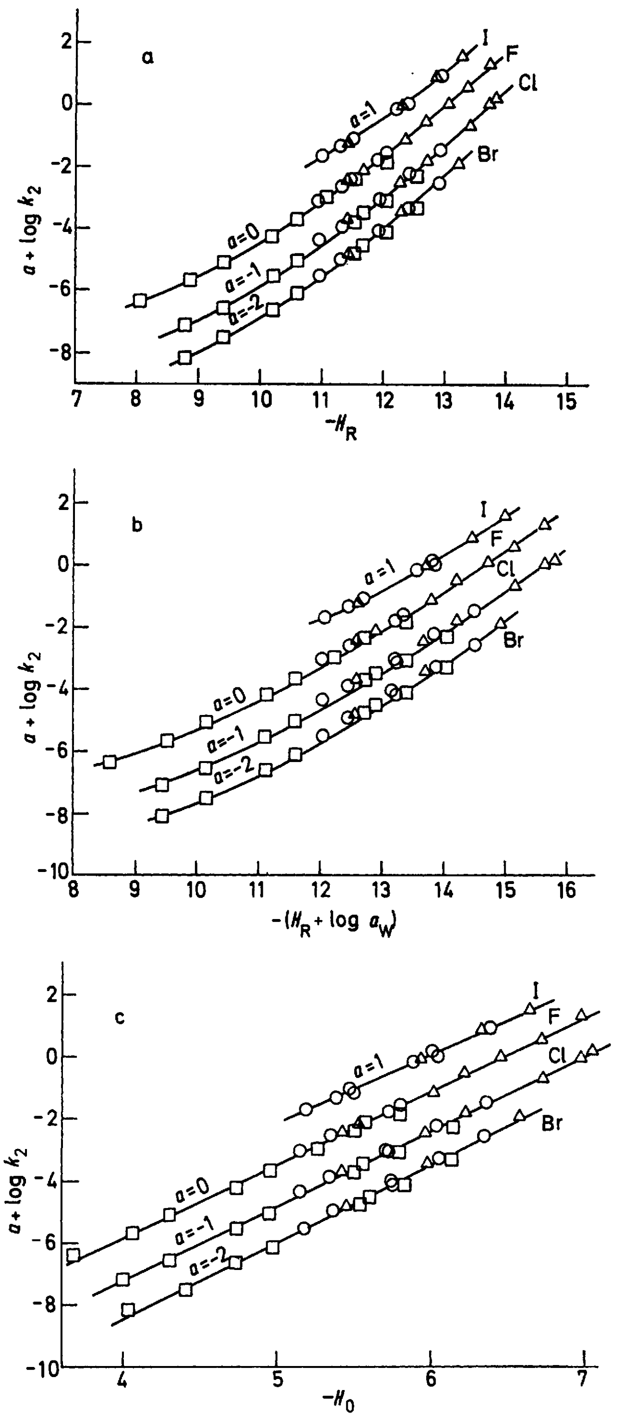

FIGURE 1 Plots of a, [$a + \log k_{2(obs)}$] against $-H_R$; b, [$a + \log k_{2(obs)}$] against $-(H_R + \log a_w)$; c [$a + \log k_{2(obs)}$] against $-H_0$ for the nitration at 25 °C in aqueous sulphuric acid of fluorobenzene (F), chlorobenzene (Cl), bromobenzene (Br), and iodobenzene (I) (△, data from ref. 8; □, data from ref. 5; ○, data from ref. 7; H_R values from ref. 9; H_0 values from ref. 11)

This suggests a further analysis of the experimental relationship (1) in terms of the nitration mechanism (4).

From equation (6), rewritten as (9), and taking (10) into account,* relation (11) can be obtained. The inequality

$$\log\frac{f_{AR}f_{NO_2^+}}{f^{\ddagger}} + \log\frac{f_{HNO_3}f_{H^+}}{f_{NO_2^+}} - n\log\frac{f_Bf_{H^+}}{f_{BH^+}} = (n-1)\log[H^+] + \log a_w + m \quad (9)$$

$$(n-1)\log[H^+] + \log a_w \neq a\log\frac{f_Bf_{H^+}}{f_{BH^+}} \quad (10)$$

$$\log\frac{f_{AR}f_{NO_2^+}}{f^{\ddagger}} + \log\frac{f_{HNO_3}f_{H^+}}{f_{NO_2^+}} \neq a\log\frac{f_Bf_{H^+}}{f_{BH^+}} \quad (11)$$

(11), however, is in sharp contrast with the linear relationship $\log f_Xf_{H^+}/f_{XH^+} = m \log f_Yf_{H^+}/f_{YH^+}$ which has been demonstrated to be true, without any exception, for a large number of acid–base equilibria of weak bases, such as triarylmethanols.[16,17]

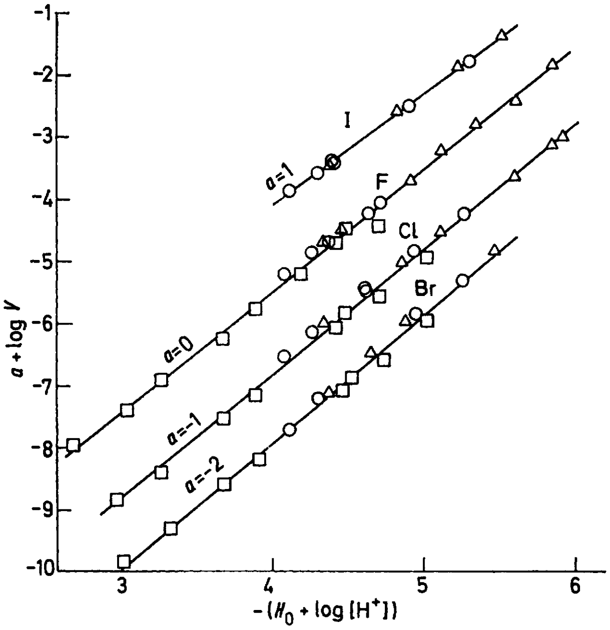

FIGURE 2 Plots of ($a + \log V$) against $-(H_0 + \log[H^+])$ {$\log V = \log k_{2(obs)} - \log[H^+] + \log a_w$} for the nitration at 25 °C in aqueous sulphuric acid of fluorobenzene (F), chlorobenzene (Cl), bromobenzene (Br), and iodobenzene (I) (△, data from ref. 8; □, data from ref. 5; ○, data from ref. 7; H_0 values from ref. 11; [H+] values from ref. 15)

It appears important then, to test relation (11) by plots $\log k_{2(obs)} - \log[H^+] + \log a_w$ against $-(H_0 + \log[H^+])$,† since $-(H_0 + \log[H^+])$, $= \log f_Bf_{H^+}/f_{BH^+}$ holds sufficiently[17] in the acidity range examined.

On the basis of the experimental results, (Figure 2) the observed straight lines are interpreted as evidence of the breakdown of relationship (11), and by extension, of the limitations of (1). The validity of equation (12) is

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* The validity of relation (10) derives from the fact that $\log[H^+]$[15] and $\log a_w$[15] are not linearly related to $-(H_0 + \log[H^+])$.

† [H+] = molar acid concentration of H+ [15] has been utilized in the experimental relationship to be verified.

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established experimentally through (13). The latter, as opposed to (1), is the only relationship consistent with a nitration model *via* a Wheland intermediate involving NO_{2^+} ions.

Agreement between (2) and (13) would follow, if the H_R function is adequate,‡ provided slopes n' of unity

$$\log \frac{f_{AR} f_{NO_2^+}}{f^{\ddagger}} + \log \frac{f_{HNO_3} f_{H^+}}{f_{NO_2^+}} = b \log \frac{f_B f_{H^+}}{f_{BH^+}} \quad (12)$$

$$\log k_{2(obs)} - \log[H^+] + \log a_w = b(H_0 + \log[H^+]) + d \quad (13)$$

were rigorously obtained. Since (13) has been derived from the nitration mechanism (4) involving non-hydrated nitric acid, it follows that the monohydrated species is not necessarily required in the nitration reactions, equation (5) being incompatible with (4).

From the results of our analysis, the main point to be emphasized is the important role of relationships (12) and (13). First their validity sets a limit to the meaning of relationships (1)—(3) as mechanistic criteria to be utilized in nitration reactions. The validity of relation (12), moreover, does provide assurance that the acid–base equilibria of the species involved in nitration will comply with the same law for activity coefficients, whichever the weak base chosen in sulphuric acid solution. This allows us to extend the applicability of M_C activity coefficient relationship[16,17] to equilibria involved in nitration, and to calculate thermodynamic nitration rates referred to the aqueous standard state.

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‡ Recently, some uncertainties involved in the overlapping procedure of arylmethanols have been pointed out.[9]