741. *Kinetics of Oxidation of Formate Ions with Bromine:
An* H_ *Acidity Function.*

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Formate ions are oxidised by bromine yielding carbon dioxide and water, according to the rate law $-d[Br_2]/dt = k_o[HCO_2^-][Br^2]$. Thus in acid solutions, the rate of oxidation of formic acid is inversely proportional to the acidity, and studies of the variation of the reaction rate with acid concentration have provided a means of determining an H_- acidity scale, which accords well with a theoretical model of electrolyte solutions.

PREVIOUS work [1] on this reaction has demonstrated that its stoicheiometry is

$$Br_2 + HCO_2^- \longrightarrow H^+ + 2Br^- + CO_2 \qquad (1)$$
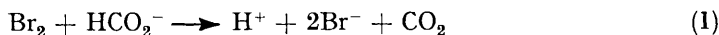
and the reaction rate is given by:

$$-d[Br_2]/dt = k_o[HCO_2^-][Br_2] \qquad (2)$$

It has been shown that salt effects on the rate of hydride ion removal from aldehyde hydrates are small,[2,3] and since this reaction is also a hydride ion removal we would not expect k_o to show a large salt effect.

Now according to the definition [4] of the H_- acidity scale we have:

$$K_a = \frac{h_-\,[HCO_2^-]}{[HCO_2H]} \qquad (3)$$

where K_a is the acidity constant of formic acid, and

$$h_- = \frac{[H^+]y_{H^+}y_{HCO_2^-}}{y_{HCO_2H}} \qquad (4)$$

where the y's are molar activity coefficients, and

$$H_- = -\log h_-, \qquad (5)$$

where H_- is the required acidity function.

Substituting eqn. (3) into (2) we obtain

$$-d[Br_2]/dt = k_e\,[HCO_2H][Br_2] \qquad (6)$$

where $\qquad\qquad k_e = k_o K_a/h_-, \qquad (7)$

k_e being the experimental second order rate constant in acid solutions (pH <1) since $[HCO_2H]$ will be equal to the analytical formate concentration. Thus if k_o and K_a are known, H_- can be determined directly by measurements of k_e in acid solutions.

RESULTS

Experimental.—The rate of disappearance of bromine during a reaction was followed at 398 mμ with a Hilger Uvispek spectrophotometer equipped with a brass cell-block whose temperature could be controlled electrically to $\pm 0\cdot1°$ at $25°$. All kinetic measurements were made at $25°$.

Determination of k_o.—Bromine concentrations used were all $\sim 5 \times 10^{-3}$M, and the small quantities of bromide produced did not significantly affect the free bromine concentration. Formic acid concentrations were $\sim 0\cdot1$M. All reactions were carried out in solutions of

[1] Hammick, Hutchison, and Snell, *J.*, 1925, **127**, 2715.
[2] McTigue and Sime, *Austral. J. Chem.*, 1963, **16**, 592.
[3] Cox and McTigue, *Austral. J. Chem.*, in the press.
[4] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

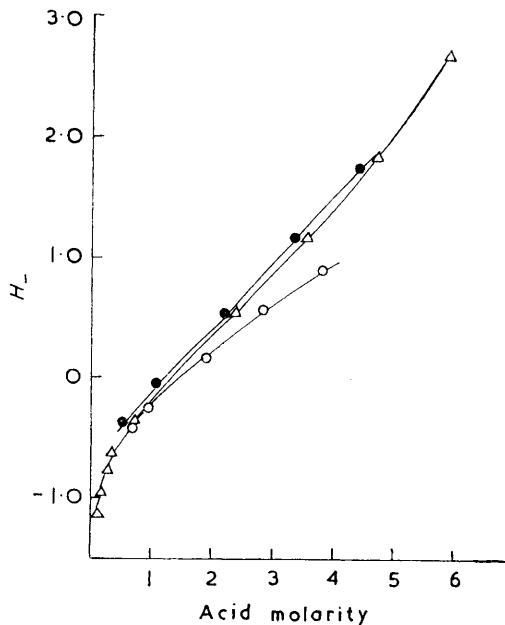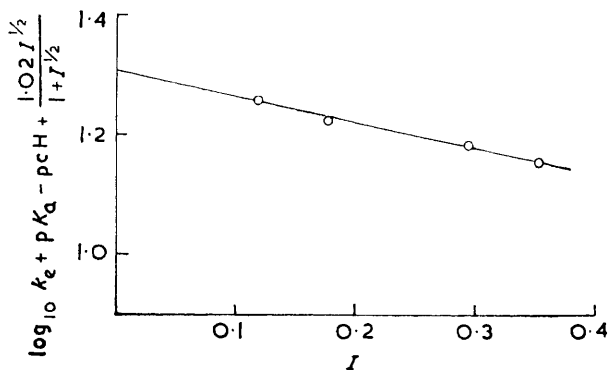Fig. 1. Determination of k_0 by extrapolation to zero ionic strength.

Fig. 2. H_- Scale for formate ions (plots of $pK_a + \log (k_e/k_0)$ against acid molarity: triangles, $HClO_4$; open circles, HNO_3; closed circles, H_2SO_4. pK_a for formic acid taken as 3·75.

Fig. 3. Comparison between theory and experiment in H_- scale for formate ions: triangles, $HClO_4$; open circles, H_2SO_4. $(X - \log a_w)$ values tabulated in ref. 5.
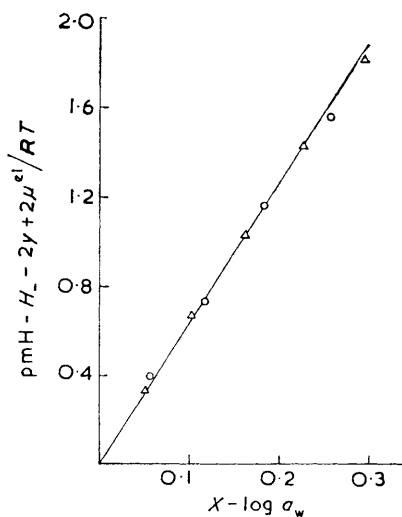
perchloric acid with $0\cdot1 \leqslant [HClO_4] < 0\cdot5M$, and the analytical formate concentration was equal to the formic acid concentration. Thus k_e was the rate constant measured experimentally. k_e showed considerable variation with ionic strength (I) in the acid concentration, range used, and in order to determine k_0, we have measured k_e as a function of ionic strength, and extrapolated to zero ionic strength. Thus from eqn. (7)

$$k_e = \frac{k_0 K_a \, y_{HCO_2H}}{[H^+] \, y_{H^+} \, y_{HCO_2}} \tag{8}$$

and we may write:

$$\log y_{H^+} \, y_{HCO_3^-} = 2 \log y_{\pm} = -\frac{1\cdot02I^{\frac{1}{2}}}{1 + \alpha I^{\frac{1}{2}}} + \beta'I \tag{9}$$

$$\log y_{HCO_2H} = \beta''I \tag{10}$$

Hence

$$\log k_e + pK_a - pcH + \frac{1\cdot02I^{\frac{1}{2}}}{1 + \alpha I^{\frac{1}{2}}} = \log k_0 + \beta I \tag{11}$$

where $\beta = \beta'' - \beta'$.

We have taken $\alpha = 1$ and plotted the left hand side of eqn. (11) against I, and have obtained a straight line of slope $\beta = -0\cdot42$, intersecting the vertical axis ($I = 0$) at $\log k_0$ (see Fig. 1). This procedure yields a value of $k_0 = 20\cdot1$ l. mole^{-1} sec.$^{-1}$ which compares well with the earlier value [1] of ~22.

Determination of H_.—In this work we have used formic acid concentrations as high as $0\cdot5M$ at high mineral acid concentrations since the reaction rate becomes extremely low at high acidities.* The results are shown in Fig. 2, and $-H_-$ values at selected molarities are given in the following Table:

Molarity	0·5	1·0	2·0	3·0	4·0	5·0	6·0
HNO₃	−0·50	−0·20	0·23	0·62	(0·95)	—	—
HClO₄	−0·52	−0·17	0·35	0·87	1·41	2·02	2·76
H₂SO₄	−0·42	−0·12	0·42	0·97	1·51	—	—

A check was made on the stability of formic acid in perchloric acid solutions in the absence of bromine. $0\cdot1M$-Formic acid in $6M$-perchloric acid showed a negligible change in u.v. spectrum in the vicinity of 200 mμ during 48 hr. at room temperature. We found evidence of oxidation of formic acid by $5M$-nitric acid, in which the rate of oxidation by the nitric acid was greater than the rate of oxidation by bromine.

Application of Theory.—A recently-developed modification [5] of Glueckauf's treatment [6] of concentrated electrolyte solutions has been applied successfully to the prediction of the Hammett (H_0) acidity function. In this modification the activity coefficient of a tracer electrolyte in a swamping electrolyte is given by:

$$2 \log \gamma_{\pm} = 2\mu_{\pm}^{el}/RT + r_{\pm}X - 2Y + h_{\pm}(X - \log_{10} a_w) \tag{12}$$

where $\gamma_{\pm}$ is a mean molal activity coefficient, $r_{\pm} = \phi_{\pm}/v_w$ where $\phi_{\pm}$ is the apparent molar volume of the tracer electrolyte and v_w is the apparent molar volume of water; $h_{\pm}$ is the total hydration number of one " molecule " of tracer electrolyte, R is the gas constant, T the absolute temperature, a_w the water activity.

$$X = \frac{0\cdot00782 \, m_s \, (r_s + h_s - 2)}{1 + 0\cdot018 \, m_s r_s} \tag{13}$$

$$Y = \log_{10} (1 + 0\cdot018 \, m_s r_s) \tag{14}$$

where m_s is the molality of the swamping electrolyte, $r_s = \phi_s/v_w$, ϕ_s being the apparent molar volume of the swamping electrolyte, and h_s is the hydration number of the swamping electrolyte.

$$\frac{\mu^{el}}{RT} = -\frac{0\cdot509I^{\frac{1}{2}}}{1 + \alpha I^{\frac{1}{2}}} + Z \tag{15}$$

for a 1 : 1 electrolyte,[6] where α is a " distance of closest approach " parameter and Z is a

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* H_- has been calculated from eqn. (7), whereby $H_- = pK_a + \log_{10} (k_e/k_0)$.

[5] McTigue, *Trans. Faraday Soc.*, 1964, **60**, 127.
[6] Glueckauf, " Structure of Electrolytic Solutions," ed. Hamer, Wiley, 1957, p. 97.

correction function which has been determined by curve-fitting and is tabulated by Glueckauf.[6] Shifting to the molal concentration scale, we have from eqn. (4):

$$\text{pmH} - H_- = \log \frac{\gamma_{\text{H}^+}\gamma_{\text{HCO}_2^-}}{\gamma_{\text{HCO}_2\text{H}}} \qquad (16)$$

which on application of eqn. (12) yields:

$$\text{pmH} - H_- - 2Y + 2\mu_{\pm}^{\text{el}}/RT = h'(X - \log_{10}a_\text{w}) \qquad (17)$$

where $h' = h_{\text{H}^+} + h_{\text{HCO}_2^-} - h_{\text{HCO}_2\text{H}}$, h_i being the hydration number of species i. $\text{pmH} = -\log m_{\text{H}^+}$ where m_{H^+} is the hydrogen-ion molality. We have taken $\alpha = 1$.

By plotting the left hand side of eqn. (17) against $X - \log_{10} a_\text{w}$ we should obtain a straight line of slope h', and such a plot for perchloric and sulphuric acid is shown in Fig. 3. An excellent straight line is obtained, passing through the origin with $h' = 6.5$. All thermodynamic data used in the calculations were taken from tables in standard texts.[7,8]

DISCUSSION

Previously the H_- acidity function has been determined for a number of strongly alkaline solutions,[9-11] using aromatic amines as indicators, and recently in perchloric and sulphuric acid using cyanocarbon acids as indicators.[12] The validity of the acidity scale given in Fig. 2 depends on the assumption that our k_0 is independant of medium. Granted this, we note that our H_- scale falls below the H_0 scale for H_2SO_4 and $HClO_4$ at low concentrations, but, in $HClO_4$, crosses the H_0 curve at $\sim 7\text{M}$. Acidity scales are now regarded as being valid only for a chemically related set of indicator bases,[13] hence the present scale should at best be applicable only to carboxylate anions.

The theoretical model is consistent with our H_- scale for H_2SO_4 and $HClO_4$ if

$$h_{\text{H}^+} + h_{\text{HCO}_2^-} - h_{\text{HCO}_2\text{H}} = 6.5$$

or, since[5,6] $h_{\text{H}^+} = 4.5$, $h_{\text{HCO}_2^-} - h_{\text{HCO}_2\text{H}} = 2$ which is reasonable. We conclude that we have established a reasonable H_- acidity scale for formate ions in sulphuric and perchloric acid, which may well apply to carboxylate ions in general. Comparing our scale with that determined with the cyanocarbon acids, we note that in 5M-acid our H_- scale is about 0.8 units more positive. Applying eqn. 17 to the cyanocarbon acid scale in perchloric acid (concentration range 0—6M) we find that good agreement between theory and experiment is obtained with $h_{\text{anion}} - h_{\text{acid}} = 2.5$ and $\alpha = 3$. A high α-value is expected in view of the large size of the anions, although 3 is perhaps physically unrealistic since it corresponds to a distance of closest approach of about 9 Å.

We conclude that H_- acidity functions, like H_0 functions,[13] are dependent on the chemical nature of the indicator bases used in establishing the scales, and the usefulness of such functions is similarly restricted.

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[7] Robinson and Stokes, " Electrolyte Solutions," Butterworth, 1955, 1st edn.
[8] Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold, 1954, 2nd edn.
[9] Schwarzenbach and Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 348.
[10] Langford and Burwell, *J. Amer. Chem. Soc.*, 1960, **82**, 1503.
[11] Stewart and O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 494.
[12] Boyd, *J. Amer. Chem. Soc.*, 1961, **83**, 4288.
[13] See *e.g.*, Katritzky, Waring, and Yates, *Tetrahedron*, 1963, **19**, 465.