

CXLIV.—*The Rate of Reaction between Formic Acid and Iodine in Aqueous Solution.*

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It has been shown (Hammick, Hutchison, and Snell, J., 1925, 127, 2715) that the rate of reaction between bromine and formic acid is represented by the mass-action equation

$$dx/dt = k[\text{H}\cdot\text{COO}'][\text{X}]/\{1 + [\text{X}']/K_1\} \dots \dots \dots (1)$$

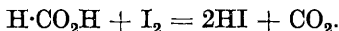
in which $[\text{X}]$ is the total concentration of free halogen $\text{X}_2 + \text{X}'_2$, $[\text{X}']$ the concentration of halogen ion, and K_1 is the equilibrium constant $K_1 = [\text{X}_2][\text{X}']/[\text{X}'_2]$. For bromine, $1/K_1$ is of the order of 10 and $[\text{Br}']/K_1$ could not be neglected in comparison with unity. In chlorine and iodine, however, we have two extreme cases. For chlorine, K_1 is large and $[\text{Cl}']/K_1$ can be neglected; for iodine, K_1 is small and has the value 1.75×10^{-3} at 45° (Fedotiev, *Z. physikal. Chem.*, 1909, 69, 22) and 1.365×10^{-3} at 25° (Jakowkin, *ibid.*, 1896, 20, 19). Hence in the case of iodine we may neglect unity in comparison with $[\text{I}']/K_1$ and we should expect to find that, whereas the rate of reaction between chlorine and formic acid would be practically independent of chlorine-ion concentration, that between iodine and formic acid would be inversely proportional to the concentration of iodine ion. That is to say,

$$dx/dt = k[\text{H}\cdot\text{COO}'][\text{I}]/\{[\text{I}']/K_1\} \dots \dots \dots (1A)$$

should represent the course of the reaction in the latter case. Iodine reacts at 60° at a convenient rate and results have been obtained at that temperature that confirm the conclusion arrived at above.

Iodine and formic acid, in the presence of potassium iodide, were mixed in a glass stoppered flask in a thermostat maintained at $61.5^\circ \pm 0.25^\circ$, the iodine being estimated from time to time with standard thiosulphate. In all experiments, the potassium iodide was present in excess (never less than 10 to 1) sufficient to eliminate perturbations due to the iodine ion produced during the reaction. A zero time-correction was obtained by plotting $\log a/(a - x)$ against time and extrapolating to zero time. The unimolecular velocity coefficients given below have been corrected in this way.

By analogy with the reaction between bromine and formic acid, it is to be expected that iodine would react as follows :



An experiment was therefore carried out by mixing equal volumes of equivalent solutions of formic acid and iodine in presence of

excess of potassium iodide and measuring the rate of disappearance of the iodine. The results show that the reaction is bimolecular, as the above equation suggests.

TABLE I.

$[\text{H}\cdot\text{CO}_2\text{H}] = N/100$. $[\text{I}_2] = N/100$. $a - x =$ thiosulphate titre at time t .

t (mins).	$a - x$.	$1/(a - x) - 1/a$.	$k \times 10^3$ (bimol. coeff.).
0.0	10.9	—	—
4.53	10.65	0.00215	4.45
10.08	10.4	0.00441	4.37
19.42	9.95	0.00826	4.51
25.6	9.7	0.01146	4.48

Influence of Formic Acid Concentration on the Rate of Disappearance of Iodine.—In Table II are the results of a series of determinations of the unimolecular velocity coefficient for two different concentrations of formic acid.

TABLE II.

$[\text{H}\cdot\text{CO}_2\text{H}]$.	$[\text{KI}]$.	$[\text{I}_2]$.	$k \times 10^3$.	
$N/3$	0.117N	0.011N	9.15	ratio = 1.34
$2N/3$	0.117	0.011	12.2	
$N/3$	0.234	0.011	4.65	" 1.37
$2N/3$	0.234	0.011	6.35	
$N/3$	0.17	0.016	5.85	" 1.45
$2N/3$	0.17	0.016	8.47	

Since formic acid obeys the dilution law, we have approximately $\alpha^2/V = K_d$, where α is the degree of dissociation, V is the dilution, and K_d is the dissociation constant; hence, for any two dilutions V_1 and V_2 , we have $\alpha_1/\alpha_2 = \sqrt{V_1/V_2}$. Thus $[\text{H}\cdot\text{COO}']_1/[\text{H}\cdot\text{COO}']_2 = (\alpha_1/V_1)/(\alpha_2/V_2) = \sqrt{V_2/V_1}$. For the pairs of velocity coefficients given in Table II, $V_2/V_1 = 1/2$ and hence $[\text{H}\cdot\text{COO}']_2/[\text{H}\cdot\text{COO}']_1 = \sqrt{2} = 1.41$. If the rate of reaction is proportional to $[\text{H}\cdot\text{COO}']$ we should expect to find that doubling the concentration of formic acid would increase the velocity coefficient in the ratio of 1 to 1.41. The mean of the ratios in Table II is 1.39.

Influence of Hydrogen-ion Concentration.—Unimolecular velocity coefficients were determined in the presence of varying quantities of hydrochloric acid. The results of a series of determinations are summarised in Table III.

TABLE III.

$[\text{HCl}]$.	α .	$[\text{H}]$.	$k \times 10^3$.	$k \times [\text{H}] \times 10^3$.
0.066N	0.844	0.06N	3.5	0.210
0.132	0.812	0.11	1.9	0.209
0.198	0.786	0.16	1.19	0.191

Under α are the activity coefficients of hydrochloric acid (Ellis, *J. Amer. Chem. Soc.*, 1916, **38**, 535; Noyes, *ibid.*, 1917, **39**, 2532).

These figures refer to acid at room temperature; in using them at 60°, we are, of course, assuming that the ratios of activity coefficients corresponding to different concentrations are independent of temperature. Under [H] are effective concentrations of hydrogen ion, calculated from the Law of Mixed Acids (Lewis, "System of Physical Chemistry," 1921, Vol. 1, p. 255) by the formula $[H] = K_a/\alpha[HCl]$; the dissociation constant for formic acid, K_a , is taken as 2.1×10^{-4} (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 239); this value refers to 18° and hence values of [H] can only be regarded as relative. Nevertheless, the constancy of the product $k \times [H]$ shows that the velocity of the reaction is inversely proportional to the effective concentration of the hydrogen ion and therefore directly proportional to the concentration of formyl ion.

Influence of Iodine-ion Concentration.—The concentration of iodine ion was varied between 0.117*N* and 0.350*N* by the addition of potassium iodide and was always in excess sufficient to mask the effect of the iodine ion produced in the course of the reaction. The results are in Table IV.

TABLE IV.

$[H \cdot CO_2H] = N/3.$				
$[I_2].$	$[KI].$	$k \times 10^2.$	$\alpha.$	$k \times \alpha \times [KI] \times 10^3.$
0.012 <i>N</i>	0.117 <i>N</i>	0.915	0.735	0.786
0.11	0.234	0.465	0.689	0.750
0.11	0.351	0.328	0.663	0.762
0.16	0.170	0.585	0.710	0.733
0.0275	0.292	0.372	0.655	0.733
0.0335	0.351	0.330	0.663	0.768

The values for the activity coefficient, α , are from McInnes and Parker (*J. Amer. Chem. Soc.*, 1915, **37**, 1445) for potassium chloride in the presence of hydrogen ion, no data being available for the activity of the iodine ion. The close similarity of the potassium chloride and potassium bromide values renders the use of potassium chloride values justifiable. The figures do not refer to 60°, and hence are assumed to be only relatively correct. The product in column 5 shows that the rate of reaction is inversely proportional to the effective concentration of the iodine ion, as predicted by equation (1A).

The reaction between iodine and sodium formate in the presence of potassium iodide has been studied by Dhar (*J.*, 1917, **111**, 726). He concludes that interaction takes place between iodine and formyl ions and notices the retarding influence of potassium iodide. He explicitly excludes, however, the possibility that this effect is due to disturbance of the equilibrium $I_2 + I' \rightleftharpoons I'_3$, and claims that the potassium iodide acts catalytically. He compares two cases in which "the concentrations of sodium formate are equal and according to

the mass-action equilibrium the velocity coefficients should be the same, since the ratio of the concentration of potassium iodide and iodine is the same in the two cases" (*loc. cit.*, p. 730). As a matter of fact, the ratio of the two velocity coefficients is $k_1/k_2 = 0.00196/0.00378 = 0.52$. If we now apply equation (1A) to the case of a velocity determination in which $[\text{H}\cdot\text{COO}']$ and $[\text{I}']$ are constant (sodium formate and potassium iodide were in excess in Dhar's experiments), we have on integrating, $(1/t) \log a/(a-x) = k = K \cdot K_1 \cdot [\text{H}\cdot\text{COO}']/[\text{I}']$. For two experiments in which $[\text{H}\cdot\text{COO}']$ is the same in each, we have $k_1/k_2 = [\text{I}']_2/[\text{I}']_1$. Applying this to Dhar's examples, with the assumption that the potassium iodide is completely dissociated, we find $k_1/k_2 = 2.7066/5.4132 = 0.50$, in excellent agreement with the ratio given above. Thus Dhar's results do not, as he concludes, require us to regard the action of the potassium iodide as catalytic, but actually provide very good evidence in support of the view embodied in equations (1) and (1A) above.

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[Received, January 28th, 1926.]