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OXIDATION OF FORMIC ACID WITH IODINE. PART I

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Abstract. The reaction between formic acid and iodine was studied, and it was found to be of first order. The calculated energy of activation is 19.3 kcal/mole.

Dhar¹ studied the oxidation of formic acid with chromic acid, also with iodine using the volumetric technique. He reported that the oxidation of formic acid is unimolecular with respect to chromic acid and termolecular with respect to formic acid. Doosaj and Bhogwat² studied the oxidation of sodium formate with iodine and found that the order of reaction with respect to sodium formate or iodine was unity, using the Ostwald isolation method. Dhar¹ used an excess of sodium acetate salt to regulate the reaction smoothly, whereas Bhogwat argued that without the addition of sodium acetate, the reaction is smooth and sodium acetate has practically no effect on the velocity constant when the sodium formate concentration is kept sufficiently high. These authors independently agreed that the reaction is retarded by the addition of potassium iodide due to the decrease in the amount of free iodine as KI_3 is formed. We have taken up this problem due to the discrepancy of Dhar and Bhogwat for the addition of sodium acetate in the reactor. The previous authors have not studied this reaction at comparatively high temperatures using a low concentration of formic acid and this investigation was therefore carried out at comparatively high temperatures. However, in a few experiments we have selected the same concentrations, under same conditions for comparison of results.

It is not surprising to find that the data obtained in this present investigation on the oxidation of formic acid with iodine differ somewhat from those reported by Dhar and Bhogwat sixty years ago. These results emphasize the fact that many of older kinetic data in the literature are in need of careful checking. In this research the volumetric and gasometric techniques have been used to compare the results.

Experimental

Chemicals

Formic acid (BDH), sodium thiosulphate, iodine and potassium iodide were of analytical reagent grade. They were used without purification.

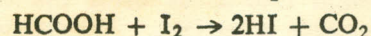
Apparatus and Techniques

Two different techniques were used.

a) The volumetric method in which the iodine was titrated with sodium thiosulphate using starch as an

internal indicator. 50 ml of known concentration of formic acid and 50 ml of known iodine solution (prepared in a fixed concentration of KI solution) were clamped in iodine flasks in a thermostat $\pm 0.08^\circ$ during the course of all the experiments. Formic acid was rapidly mixed in the iodine solution and after vigorous shaking 10 ml of the mixture were withdrawn in a clean conical flask which were previously half dipped in ice-cold water to quench the reaction. The solution was titrated immediately with sodium thiosulphate solution, using starch as an indicator. The reaction was followed at regular time intervals and the volume of iodine consumed was determined (Table 1).

(b) A gasometric method was used in which the volume of carbon dioxide evolved according to the equation was measured with respect to time.



The CO_2 was collected at regular time intervals. These experiments were conducted in a constant temperature thermostat $\pm 0.08^\circ$ by measuring the volume of CO_2 produced at constant pressure based upon the actual molar volume of CO_2 as described in previous articles.^{4,5} A weighed amount of formic acid was sealed in a thin glass bulb which could be easily broken in the reactor in iodine solution. The CO_2 was collected at room temperature in a micro-burette filled with water which had been previously saturated with CO_2 . Several experimental runs were made at different temperatures with different concentrations of formic acid, keeping the ionic strength constant. The effect of KI salt was studied at 80° and the results are tabulated in Table 5.

For every set of experiments the volume of CO_2 evolved was plotted against time which resulted in a smooth parabolic curve. The $\log(V_\infty - V_t)$ vs time was linear over practically the entire course of the reaction indicating that the reaction is of first order where V_∞ represents the maximum yield of CO_2 (98.8% of the theoretical value) in all the experiments and V_t is the amount of gas at any time t , where 0.023 g formic acid was enough to produce 11.8 ml of CO_2 at STP. Potassium iodide concentration was also varied to study the effect of salt on the rate of reaction. A plot of the total ionic strength $\sqrt{\mu}$ against $\log K$ in Table 5 shows a linear relationship.

The gasometric method was preferred to study

the reaction mechanism as the volumetric method always gave decreasing rate constants at each temperature due to the large surface area and hydrogen ions which are probably responsible for retarding the reaction.

Discussion

The rate constants for the oxidation of formic acid with iodine were studied by a titration method between the range 40–70°. The rate values of Table 1 give an idea of the irregularity of the reaction. Dhar used sodium acetate to make the reaction velocity regular, but Bhogwat's argument was that without the addition of sodium acetate the reaction velocity is regular. Our experimental results show that both the above statements are not correct as several experiments were conducted and failed to yield constant rate values as shown by the experimental data cited in Table 1. The values of the rate constants for the same concentration of the reactants of Table 1, carried out at different temperatures, calculated at 60 min time interval at each run temperature are shown in Table 2. A graph of $\log K$ against $1/T$ resulted in a straight line giving an energy of activation of 12.8 kcal/mole. Again the rates were calculated at one hundred minutes at each temperature and a plot of $\log K$ against $1/T$ yielded an energy of activation of 12.5 kcal/mole. This indicates that the constant retarding effect continues with time at all the temperatures. We concluded that one cannot obtain constant rate values using the volumetric technique for such a reaction. The results of Dhar were also plotted which gave the energy of activation of 11.4 kcal/mole. This suggests that it cannot be accounted for by experimental error since the values of the energy of activation reported by previous authors are in close agreement with ours. Although we repeated the experiments of Dhar and Bhogwat, we still failed to get the constant rate values, we then decided to follow the gasometric method in order to obtain better experimental results to study the reaction mechanism. Doosaj and Bhogwat reported that light has little effect on the reaction velocity. This indicates that the constant error may be due to hydrogen ions and that may be the reason Dhar used sodium acetate to make the reaction regular.

In our experimental method (B), 20.0 ml of the reaction mixture were used to reduce the surface area and the hydrogen ions. The rate constants obtained by this technique are fairly constant and reproducible. The volume of CO_2 and time plots gave the smooth parabolic curve. Experiments at each temperature were repeated a sufficient number of times to obtain complete assurance of their validity and reproducibility. In this investigation the $\log (V_{\infty} - V_t)$ was a linear function of time over practically the entire course of the reaction. This indicates that the reaction is of first order with respect to formic acid.

The average rate constants were calculated in the usual manner from the slopes of the experimental logarithmic plots. The parameters of the Eyring

equation based upon the data in Table 3 are shown in Table 4. The energy of activation calculated by this method is 19.3 kcal/mole. The entropy of activation is -18.7 cal/mole/deg. We expected a somewhat more negative entropy of activation as the reactants dissociate into ions. However, the large negative entropy of activation may be attributed to the formation of, an intermediate complex formed between the formate ion and the iodide ion. Since the frequency factor is proportional to $e\Delta^{\ddagger}/R$, it follows that the frequency

TABLE 1. (HCOOH 0.0255 MOL/L, I_2 0.0504 MOL/L, $\text{Na}_2\text{S}_2\text{O}_3$ 0.01 N 50.0 ML, $\text{HCOOH} + 50.0$ ML I_2 , KI 0.1 MOL IN 100 ML MIXTURE.

Time (min)	$\text{Na}_2\text{S}_2\text{O}_3$	Concn of I_2	Concn of HCOOH (0.00637 mol/l)	$K \times 10^4$ (sec $^{-1}$)
20	23.1	0.0232	0.00420	3.47
40	21.9	0.0213	0.00386	2.07
60	20.3	0.0204	0.00375	1.09
80	19.5	0.0195	0.00355	1.22
100	19.1	0.0192	0.00348	1.01
120	18.7	0.0188	0.00339	0.88
140	18.2	0.0183	0.00314	0.84

TABLE 2. THE RATE CONSTANTS FOR THE CONCENTRATION OF THE TABLE 1 OBTAINED AT DIFFERENT TEMPERATURES AND THE RATE CONSTANTS AT 60 MIN INTERVAL.

Temp	$K \times 10^4$ (sec $^{-1}$)	Temp coeff
40	1.028	—
50	1.091	1.061
60	1.159	1.062
70	1.225	1.057

TABLE 3. RATE CONSTANTS OBTAINED AT FOUR TEMPERATURES BY GASOMETRIC METHOD.

Temp	$K \times 10^4$ (sec $^{-1}$)	Temp coeff
70	3.157	} 2.22 2.15
75	4.677	
80	6.998	
85	10.06	

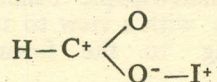
TABLE 4. THERMODYNAMIC PARAMETERS CALCULATED FROM THE DATA OF TABLE 3.

K (sec $^{-1}$)	E. kcal/mole	$\log A_{-1}$ (sec $^{-1}$)	ΔF^{\ddagger} kcal/mole	ΔH^{\ddagger} kcal/mole	ΔS^{\ddagger} cal/mole/deg
3.157×10^4 at 70°	19.3	8.77	25.72	18.62	-18.71
6.998×10^4 at 80°	19.3	8.76	25.90	18.61	-18.66

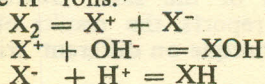
TABLE 5. RATE CONSTANTS AND THE TOTAL IONIC STRENGTH AT 80°.

μ	$\sqrt{\mu}$	$K \text{ (sec}^{-1}) \times 10^4$	KI
0.0260	0.161	6.22	0.127
0.0430	0.206	5.83	0.230
0.0650	0.255	5.29	0.377
0.0968	0.311	4.87	0.627

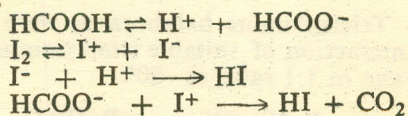
factor should decrease. The low value of the frequency factor is evidently along the right line and the complex is not disordered. The intermediate complex may be in the following form.



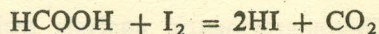
The results suggest that formic acid dissociates into H^+ ions and HCOO^- ions which associate with I^+ ions. It was assumed that I^+ ions seems to have originated in the hypothesis⁶ that when a halogen is hydrolysed, the molecules breakup into positive and negative ions, of which the former combines with the negative hydroxyl and the latter with the positive H^+ ions.⁷



Hence our proposed mechanism may be in the following form :



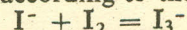
Adding the above equations, the net reaction will be :



Hence this is the equation representing the chemical change. The reaction is of first order with respect to formic acid and the overall order is

two. In the oxidation of formic acid with iodine, undissociated formic acid is inactive and the formate ions are active. The CO_2 gas is obtained from the formate ion and not from the formic acid. Hence the reaction mechanism is justified.

The addition of KI salt lowers the rate of reaction which is due to the formation of KI_3 . It shows that KI ionizes to K^+ and I^- which forms triiodide ion according to the equation.



which associates with K^+ forming KI_3 . In such a transfer of ions, rate of reaction should be irregular, but no exact proof could be obtained. The temperature coefficient of Table 3 is fairly constant, similar to that of Table 2, and it is about half of it. This shows that the effect of hydrogen ion concentration has greater retarding effect on the velocity of the reaction if the surface area is great.

Clark⁸ reported the enthalpy and entropy of activation for the decomposition of formic acid is 24.63 kcal/mole and -21.4 cal/mole/deg respectively which are close to our experimental values.

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