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On the Kinetics of the Oxidation of Formic Acid by Chlorine

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The kinetics of the oxidation of formic acid by chlorine has previously been investigated by Gróh in 1912[1] and Shilov and Slyadnev in 1948[2]. Gróh reports only a few experiments in 0.05—0.1 *M* solution of nitric acid. Gróh supposed that the reaction takes place between chlorine and formate ion in a similar way as the reaction between bromine and formic acid[3], thus

$$Cl_2 + HCOO^- \rightarrow H^+ + 2Cl^- + CO_2 \qquad (1)$$

and this mechanism is evidently in harmony with his experiments. Shilov and Slyadnev carried out experiments in 0.1—0.5 *M* solution of hydrochloric acid, and found that the reaction takes place only partly in accordance with Gróh's assumptions. Therefore the authors also claimed a reaction between free acid and chlorine:

$$Cl_2 + HCOOH \rightarrow 2H^+ + 2Cl^- + CO_2 \qquad (2)$$

which takes place simultaneously with the reaction (1). It will be shown in this paper that this claim is not substantiated by the experiments of the author.

THEORETICAL PART

To the two above mentioned reactions correspond the following two expressions for the velocity

$$-\frac{d[Cl_2]}{dt} = k_1[Cl_2][HCOO^-] \qquad (I)$$

$$-\frac{d[Cl_2]}{dt} = k_2[Cl_2][HCOOH] \qquad (II)$$

In the experiments the total concentration of chlorine was determined iodometrically. It is therefore necessary to introduce this concentration as well as the total concentration of formic acid in the expressions above.

Formic acid is dissociated in solution, thus

$$\mathrm{HCOOH} \rightleftharpoons \mathrm{H}^+ + \mathrm{HCOO}^-$$

and in the equilibrium we have

$$\frac{[\mathrm{H}^+][\mathrm{HCOO}^-]}{[\mathrm{HCOOH}]} = K_F$$

where K_F stands for the concentration equilibrium constant.

Formic acid has $K_S = 1.77\ 10^{-4}$ at 25° C [4]. From the expression $\mathrm{p}K_F = \mathrm{p}K_S + \log f_{A^-} f_{H^+}$ in connexion with the expressions of Harned and Owen, and Bjerrum and Unmack [5] for the activity coefficients of formate ion and hydrogen ion, respectively, we get $K_F = 2.34\ 10^{-4}$ at an ionic strength of 0.98. This ionic strength was used in the experiments from which the velocity constants k_1 were calculated. In the solution the equilibrium

$$\mathrm{Cl_2} + \mathrm{HOH} \rightleftharpoons \mathrm{H}^+ + \mathrm{Cl}^- + \mathrm{HOCl}$$

is certainly established. Denoting this hydrolysis constant by K_H we have

$$\frac{[\mathrm{H}^+][\mathrm{Cl}^-][\mathrm{HOCl}]}{[\mathrm{Cl_2}]} = K_H$$

From the expressions above in connexion with

$$[\mathrm{Cl_2}] + [\mathrm{HOCl}] = [\text{total chlorine}] = \mathrm{C}$$

$$[\mathrm{HCOOH}] + [\mathrm{HCOO}^-] = [\text{total formic acid}] = \mathrm{F}$$

we find for the two cases respectively

$$-\frac{d[\mathrm{Cl_2}]}{dt} = k_1 \frac{[\mathrm{H}^+][\mathrm{Cl}^-]\ K_F}{(K_H + [\mathrm{H}^+][\mathrm{Cl}^-])\ (K_F + [\mathrm{H}^+])}\ \mathrm{CF} \qquad \text{(I)}$$

$$-\frac{d[\mathrm{Cl_2}]}{dt} = k_2 \frac{[\mathrm{H}^+]^2[\mathrm{Cl}^-]}{(K_H + [\mathrm{H}^+][\mathrm{Cl}^-])\ (K_F + [\mathrm{H}^+])}\ \mathrm{CF} \qquad \text{(II)}$$

The effects of the reaction $\mathrm{Cl_2} + \mathrm{Cl}^- \rightleftharpoons \mathrm{Cl_3^-}$ are negligible.

On account of the information obtained from the papers referred to above about the kinetic of the reaction, the attention was concentrated on the expression (I).

In strongly acid solution the hydrolysis of chlorine is negligible, so we may use the total concentration of chlorine directly in the expression (I). We then get

$$-\frac{\mathrm{d}[\mathrm{Cl}_2]}{\mathrm{d}t} = k_1 \frac{K_\mathrm{F}}{K_\mathrm{F} + [\mathrm{H}^+]} \mathrm{CF}$$

and from this expression we get

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1 \frac{K_\mathrm{F}\ (a-x)\ (b-x)}{K_\mathrm{F} + (h + 2x)}$$

where h represents the initial concentration of hydrogen ion, a of total chlorine and b of total formic acid.

After integration we get the following expression

$$k_1 t = \frac{1}{a-b} \left((1 + \frac{h + 2a}{K_\mathrm{F}}) \ln \frac{a-x}{a} + (1 + \frac{h + 2b}{K_\mathrm{F}}) \ln \frac{b}{b-x} \right) \quad \text{(III)}$$

If we in this expression denote

$$\left(1 + \frac{h + 2a}{K_\mathrm{F}}\right) \frac{1}{a-b} = r_1$$

and

$$\left(1 + \frac{h + 2b}{K_\mathrm{F}}\right) \frac{1}{a-b} = r_2$$

we get

$$\mathrm{f}(x) = k_1 t = r_1 \ln \frac{a-x}{a} + r_2 \ln \frac{b}{b-x}$$

which has been used for computing k_1. As will be seen from the tables, this expression agrees rather well with the experiments.

EXPERIMENTAL PROCEDURE

All experiments were carried out at 25° C. On account of the volatility of the chlorine it was necessary to use an apparatus from which specimens could be taken with only a small loss of chlorine. The apparatus, which was used, is shown in Fig. 1. It had a volume of 1 020 ml, and was filled with one litre of a solution of chlorine. This solution was prepared by dissolving chlorine in a stock solution, which in these experiments consisted of a solution of sodium chloride and hydrochloric acid.

20 ml of the solution was taken out and used for determining the initial concentration of total chlorine. The reaction was started by adding 20 ml of a known solution of formic acid to the solution mentioned above. The time t was measured from the moment when

half of the formic acid was added. Immediately after adding the formic acid, the solution was mixed thoroughly by the 20 ml air which remained over the solution and carbon dioxide gas with a pressure of a little more than one atmosphere was put over the solution. From time to time specimens were taken out by drawing off part of the solution, about 40 g, in a tared flask containing a solution of potassium iodide. The quantity was weighed and the chlorine was titrated by 0.05 *N* solution of sodium thiosulphate. As the volume over the solution becomes greater during the experiments a small loss of chlorine cannot be avoided by this method.

Reagents. The formic acid used for the experiments was conc. formic acid *pro analysi* (Riedel-de Haën) which proved to have a boiling point of 100.7° C and a freezing point of 8.2° C. The literature quotes 100.75° C [6] and 8.4° C [7]. The chlorine was taken from a bomb, and washed by water before it was used for experiments. All the other chemicals were *pro analysi*. The water was redistilled before being used for experiments.

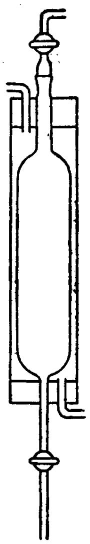

Fig. 1. Shape of experimental arrangement.

Experimental. In strongly acid solution the rate of reaction has been investigated in experiments with nearly the same initial concentrations of chlorine, formic acid and chloride ion, but the hydrogen ion concentration was varied from 0.05—0.5 *M*. To keep the ionic strength practically constant sodium chloride was added, so the concentration of chloride ion was 0.98. The experimental results from an experiment at 25° C in a solution which is 0.098 *M* as to hydrogen ion and 0.98 *M* as to chloride ion are in Table 1. In column 5 are the values of $f(x) = r_1 \ln \frac{a-x}{a} + r_2 \ln \frac{b}{b-x}$. These values were plotted against the corresponding t values and a straight line was fitted to the points. From its slope k_1 is calculated. In column 6 are the values of $t = \frac{1}{k_1} f(x)$. A comparison of column 1 and 6 shows that the assumed mechanism agrees with the kinetic experiment. The disagreement at 140 and 150 minutes is probably due to the systematic error mentioned above.

The results from all the experiments in strongly acid solution are in Table 2. In the tables the concentrations of chlorine are corrected by multiplying them by the specific gravity ϱ of the solutions, because the concentrations determined by the experimental procedure are not moles per litre but moles per 1 000 g of the solution. As the specific gravity of the solutions at 25° C did not exceed 1.04, the corrections are small.

The values of k_1 are in column 5, Table 2. They are a little different in the two series of experiments, but it has not been possible to trace the difference. It is obvious that k_1 is independent of the concentration of hydrogen ion *i.e.*

Table 1. The reaction between chlorine and formic acid at 25° C in solution 0.098 M as to hydrogen ion and 0.98 M as to chloride ion. In column 5 is given $f(x) = r_1 \ln \frac{a-x}{a} + r_2 \ln \frac{b}{b-x}$*; the constant* k_1 *is determined graphically* $k_1 = 481$*;* $t_{\text{calc.}} = \frac{1}{481} f(x)$*.* $r_1 = 5.717 \cdot 10^4$*;* $r_2 = 4.868 \cdot 10^4$*.*

1	2	3	4	5	6
t min. obs.	$a-x$	x	$b-x$	$f(x) 10^{-4}$	t min. calc.
0	0.02030	0	0.00994		
3	0.01971	0.00059	0.00935	0.129	2.7
10	0.01847	0.00183	0.00811	0.450	9.4
20	0.01713	0.00317	0.00677	0.899	18.7
30	0.01605	0.00425	0.00569	1.372	28.5
40	0.01510	0.00520	0.00474	1.913	39.8
50	0.01439	0.00591	0.00403	2.427	50.5
60	0.01388	0.00642	0.00352	2.880	59.9
70	0.01340	0.00690	0.00304	3.392	70.5
80	0.01305	0.00725	0.00269	3.836	79.8
90	0.01271	0.00759	0.00235	4.343	90.3
100	0.01243	0.00787	0.00207	4.833	100.5
110	0.01222	0.00808	0.00186	5.256	109.3
120	0.01201	0.00829	0.00165	5.740	119.3
130	0.01181	0.00849	0.00145	6.273	130.4
140	0.01163	0.00867	0.00127	6.831	142.0
150	0.01148	0.00882	0.00112	7.368	153.0

the velocity is inversely proportional to the hydrogen ion concentration even in strongly acid solution. There is thus no evidence for the reaction

$$Cl_2 + HCOOH \rightarrow 2H^+ + 2Cl^- + CO_2 \qquad (2)$$

as asserted by Shilov and Slyadnev.

An experiment in 0.1 *M* sodium hydroxide and 0.98 *M* sodium chloride showed a very small consumption of chlorine, even after several days and nights, so we can regard the velocity as practically nil. From this experiment it is evident that the hypochlorite ion does not react with the formate ion.

There remains then the question about any possible reaction between hypochlorous acid and formic acid and formate ion, respectively. An attempt has been done to explain the kinetics in weakly acid and basic solution, but the results from these experiments will be dealt with in a following paper.

Table 2. The results from experiments in strongly acid solution. Column 5 shows that the constant k_1 is independent of the concentration of hydrogen ion i.e. the velocity is inversely proportional to the concentration of hydrogen ion.

1	2	3	4	5
Initial conc. total chlorine	Initial conc. H^+	Initial conc. Cl^-	$[Na^+]$	k_1
I 0.0182	0.490	0.98	0.490	500
II 0.0207				465
I 0.0228	0.196	0.98	0.784	485
II 0.0237				503
I 0.0150	0.098	0.98	0.882	500
II 0.0203				481
I 0.0240	0.049	0.98	0.931	460
II 0.0233				494

Initial conc. formic acid = 0.01 Mean: 486

SUMMARY

The oxidation of formic acid by chlorine has been investigated at 25° C in strongly acid solution and strongly basic solution. It is shown that the experimental results in strongly acid solution can be calculated from the expression $k_1 t = \mathrm{f}(x) = r_1 \ln \frac{a-x}{a} + r_2 \ln \frac{b}{b-x}$ where a and b are the initial total concentrations of chlorine and formic acid respectively, and $r_1 = \left(1 + \frac{h+2a}{K_F}\right) \frac{1}{a-b}$, $r_2 = \left(1 + \frac{h+2b}{K_F}\right) \frac{1}{a-b}$ in which h represents the initial concentration of hydrogen ion.

From the experiments in strongly acid solution it is obvious, that the rate of reaction is inversely proportional to the hydrogen ion concentration, and in consequence of this circumstance the reaction takes place between Cl_2 and $HCOO^-$:

$$Cl_2 + HCOO^- \rightarrow H^+ + 2Cl^- + CO_2$$

in agreement with the results of Bognár for the reaction between bromine and formic acid, and the results Gróh reports in his paper, while there is no evidence for a reaction between Cl_2 and HCOOH as claimed by Shilov and Slyadnev.

An experiment in strongly basic solution shows that hypochlorite ion does not react with formate ion.

The velocity constant $k_1 = 486$ mole litre^{-1}min.$^{-1}$ at 25° C is in agreement with the value $k = 431$ stated by Gróh.

REFERENCES

1. Gróh, J. *Z. physik. Chem.* **81** (1913) 695.
2. Shilov, E. A., and Slyadnev, A. I. *Zhur. Fiz. Khim.* **22** (1948) 1312.
3. Bognár, G. *Z. physik. Chem.* **71** (1910) 529.
4. Harned, H. S., and Owen, B. B. *J. Am. Chem. Soc.* **52** (1930) 5088.
5. Bjerrum, N., and Unmack, A. *Kgl. Danske Videnskab. Selskab Mat.-fys. Medd.* **9** No. 1 (1929) 78.
6. Lecat, M. *Ann. soc. sci. Bruxelles Sér. B.* **49** (1929) 19.
7. Timmermans, J., and Hennaut-Roland *J. chim. phys.* **27** (1930) 420.

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