CLXVI.—*The Reduction of Mercuric Chloride by Sodium Formate.**

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THE reduction of mercuric chloride was proposed by Portes and Ruyssen (*Compt. rend.*, 1876, **82**, 1504) as a method for the quantitative determination of formic acid and formates; and it was pointed out at a later time by Scala (*Gazzetta*, 1890, **20**, 393) that the method could be employed for the quantitative determination of formic acid in the presence of acetic and butyric acids. It was, however, shown by Lieben (*Monatsh.*, 1893, **14**, 750) that Scala's method is accurate only when five to six times the theoretical quantity of mercuric chloride is employed and when the mixture is

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* The present (preliminary) communication is an abstract of part of a thesis submitted by one of the authors for the degree of M.Sc. of the University of Wales. This abstract is published at the present time on account of a communication having recently been made by G. A. Linhart (*Zeitsch. anorg. Chem.*, 1913, **82**, 1) on the reduction of mercuric chloride by phosphorous acid.

heated for six to eight hours on a water-bath. The reaction he represented by the equation:

$$2HgCl_2 + KCHO_2 = 2HgCl + KCl + HCl + CO_2.$$

The present investigation was undertaken with the object of studying this reduction process more fully, and a number of experiments were carried out for the purpose of obtaining information with regard to the kinetics of the reaction. This seemed to be of all the greater interest by reason of the fact that the process of reduction of mercuric chloride by phosphorous acid had been the subject of investigation by Montemartini and Egidi (*Gazzetta*, 1902, **32**, ii, 182), who, however, arrived at no definite conclusion with regard to the order of the reaction. An investigation by Garner, Foglesong and Wilson (*Amer. Chem. J.*, 1911, **46**, 361), published after an investigation had been commenced, was equally unsatisfactory; but, recently, Linhart (*Zeitsch. anorg. Chem.*, 1913, **82**, 1) has shown that the reaction is a bimolecular one.

The reduction of silver acetate by sodium formate was studied by Noyes and Cottle (*Zeitsch. physikal. Chem.*, 1898, **27**, 579), who concluded that the reaction was of the third order.

Although we have carried out experiments at 40°, 50°, 60°, 70°, and 85·5°, we shall, in the present communication, give the results only of the experiments at 40°.

EXPERIMENTAL.

The method employed was to mix 100 c.c. of a solution of sodium formate (the concentration of which was determined by means of permanganate) with 100 c.c. of a solution of mercuric chloride, both at the temperature of the thermostat (40°). After given intervals of time, 10 c.c. of the mixture were removed by means of a pipette fitted with a small filtering plug, and run into excess of a standard solution of potassium iodide. The excess of iodide was then titrated by means of a standard mercuric chloride solution.

On calculating the values of the velocity-coefficient according to the equation for a reaction of the second order, it was found that the values gradually diminished. As it had been found that the reduction of mercuric chloride by formic acid took place more slowly than with sodium formate, the falling off in the values of the velocity-coefficient was attributed to the formation of hydrochloric acid (hydrion) during the reaction. A quantity of sodium acetate was therefore added to the mixture, and this was found to render the values of the velocity-coefficient more constant.

In table I are given the detailed results obtained in one experiment and in table II are summarised the results of other experiments carried out with different initial concentrations of the reacting substances. In each case a represents the initial concentration of mercuric chloride in mols. per litre, and b the concentration of sodium formate. The values under K_2 are calculated by means of the equation:

$$K_2 = \frac{2{\cdot}30}{t(a-b)} \cdot \log_{10}\frac{b(a-x)}{a(b-x)},$$

and those under K_3 by the equation:

$$K_3 = \frac{1}{t} \cdot \frac{1}{(b-a)^2}\left\{\frac{(b-a)x}{a(a-x)} + 2{\cdot}30 \log_{10}\frac{b(a-x)}{a(b-x)}\right\}.$$

The time is expressed in hours.

Table I.

$a = 0{\cdot}1040$; $b = 0{\cdot}3685$.

t.	$a-x$.	x.	$b-x$.	K_2.	K_3.
0·3	0·0932	0·0108	0·3557	1·018	10·24
0·6	0·0831	0·0209	0·3476	1·044	11·29
0·9	0·0756	0·0284	0·3401	1·000	11·41
1·2	0·0693	0·0347	0·3338	0·966	11·53
1·6	0·0613	0·0427	0·3258	0·957	12·29
2·0	0·0553	0·0487	0·3198	0·913	12·52
2·3	0·0509	0·0531	0·3154	0·922	13·04
2·7	0·0461	0·0579	0·3106	0·904	13·51
3·0	0·0429	0·0611	0·3074	0·887	13·91
5·1	0·0260	0·0780	0·2905	0·852	18·17
			Mean...........	0·95	12·7

Table II.

			Mean.	
	Initial concentrations.	Extreme values.	K_2.	K_3.
1.	$a=0{\cdot}1040$; $b=0{\cdot}3685$...	K_2: 1·018—0·852	0·95	—
		K_3: 18·17—10·24	—	12·7
2.	$a=0{\cdot}1040$; $b=0{\cdot}1889$...	K_2: 0·861—0·791	0·83	—
		K_3: 9·10—11·50	—	10·4
3.	$a=0{\cdot}1040$; $b=0{\cdot}5637$...	K_2: 1·18—0·93	1·02	—
		K_3: 10·41—16·70	—	13·4
4.	$a=0{\cdot}1028$; $b=0{\cdot}3790$...	K_2: 1·05—0·875	0·96	—
		K_3: 10·79—13·50	—	12·2
5.	$a=0{\cdot}1028$; $b=0{\cdot}7802$...	K_2: 1·07—8·15	0·92	—
		K_3: 10·00—16·04	—	13·3
6.	$a=0{\cdot}1028$; $b=1{\cdot}0227$...	K_2: 1·18—1·01	1·11	—
		K_3: 13·03—16·90	—	15·2
7.	$a=0{\cdot}1034$; $b=0{\cdot}1737$...	K_2: 0·991—0·834	0·90	—
		K_3: 10·12—14·40	—	12·2
8.	$a=0{\cdot}1034$; $b=0{\cdot}1737$...	K_2: 1·011—0·851	0·88	—
		K_3: 9·73—14·83	—	11·9
9.	$a=0{\cdot}0503$; $b=0{\cdot}1737$...	K_2: 0·913—0·839	0·87	—
		K_3: 17·40—27·58	—	23·8
10.	$a=0{\cdot}1382$; $b=0{\cdot}1737$...	K_2: 1·01—0·862	0·91	—
		K_3: 7·86—9·91	—	9·0
11.	$a=0{\cdot}1366$; $b=0{\cdot}1739$...	K_2: 1·07—0·968	0·99	—
	(2·9 grams of sodium acetate in 200 c.c. of mixture)	K_3: 8·21—11·49	—	10·1

TABLE II.—*continued.*

Initial concentrations.	Extreme values.	Mean. K_2.	Mean. K_3.
12. $a=0\cdot1366$; $b=0\cdot1189$...	K_2: 1·09 — 1·00	1·04	—
(3·5 grams of sodium acetate in 200 c.c. of mixture)	K_3: 8·49 — 9·71	—	9 2
13. $a=0\cdot0925$; $b=0\cdot1454$...	K_2: 1·09 — 0·991	1 02	—
(3·6 grams of sodium acetate in 200 c.c. of mixture)	K_3: 12·74 —16·97	—	14·3
14. $a=0\cdot0688$; $b=0\cdot2942$...	K_2: 1·07 — 0·969	1·02	—
(1·8 grams of sodium acetate in 200 c.c. of mixture)	K_3: 18·4 —27·21	—	22·1

Even although in any given case the values of the velocity-coefficient vary during the course of the reaction, whether the coefficient be calculated according to the equation for a reaction of the second or of the third order, the mean values obtained with different initial concentrations are quite obviously more constant in the former case; and more especially is this true when sodium acetate is added to the reaction mixture. From these values, then, the conclusion may be drawn that the reduction of mercuric chloride by sodium formate is a bimolecular reaction.

This conclusion is also borne out by the application of the van't Hoff differential method of determining the order of a reaction, as is shown by the numbers in table III.

TABLE III.

I. $b=0\cdot1737$.

t.	a_1.	da_1/dt.	t.	a_2.	da_2/dt.	n.
0	0·1034	0·0118	0	0·0503	0·0059	0·96
3	0·0679		3	0·0326		
0	0·1382	0·0134	0	1·0227	0·0648	0·76
4	0·0845		4	0·9579		

II. $a=0\cdot1028$.

t.	a_1.	da_1/dt.	t.	a_2.	da_2/dt.	n.
0	0·3790	0·02323	0	1·0227	0·0648	0·99
2·2	0·3279		1	0 9579		
0	0·3790	0·02323	0	0·7802	0·0522	1·07
2·2	0·3279		1	0·7280		

These numbers show, then, that the reaction is unimolecular with reference both to mercuric chloride and to sodium formate.

That the reaction is unimolecular with reference to mercuric chloride was also found by the method of integration for the same fractional parts of the reacting substance.

For constant concentration of sodium formate ($b=0\cdot1737$) and varying concentrations of mercuric chloride ($a_1=0\cdot1603$, $a_2=0\cdot1034$; $a_3=0\cdot0503$) the following values of the time required for a given fraction of the reaction to take place were found:

$$\text{For } (a-x) = \tfrac{1}{3}\begin{cases} t_1 = 3{\cdot}35 \\ t_2 = 2{\cdot}85 \\ t_3 = 2{\cdot}80 \end{cases} \qquad \begin{aligned} t_1 : t_2 &= 1{\cdot}17 \\ t_1 : t_3 &= 1{\cdot}19 \\ t_2 : t_3 &= 1{\cdot}02 \end{aligned}$$

$$\text{For } (a-x) = \tfrac{1}{2}\begin{cases} t_1 = 6{\cdot}5 \\ t_2 = 5{\cdot}4 \\ t_3 = 5{\cdot}0 \end{cases} \qquad \begin{aligned} t_1 : t_2 &= 1{\cdot}2 \\ t_1 : t_3 &= 1{\cdot}3 \\ t_2 : t_3 &= 1{\cdot}08 \end{aligned}$$

It appears then, to be established that the reduction of mercuric chloride by sodium formate is a reaction of the second order, and as the complete reaction appears to be represented by the equation:

$$2HgCl_2 + NaCHO_2 = 2HgCl + NaCl + HCl + CO_2,$$

it follows that the reaction must take place in stages.

A similar conclusion has just been arrived at by Linhart (*loc. cit.*) for the reduction of mercuric chloride by phosphorous acid, the order of the reaction in this case being explained on the assumption that the slow reaction which is measured is the oxidation of the phosphorous acid to hypophosphoric acid. That a similar explanation can be offered in the case of the reduction of mercuric chloride by sodium formate appears to be very doubtful; but as the investigation is still in progress we shall defer the discussion of the mechanism of the reaction until the experiments which are at present in progress have been completed.

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