THE EFFECT OF CAUSTIC ALKALI ON THE OXIDATION OF STANNOUS CHLORIDE WITH AIR.

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S. W. Young[1] studied the effect of many substances on the oxidation of stannous chloride solution with free oxygen, but he did not studied the effect of alkali. The present research was carried out to know the effect of alkali by a modified method in connection with the former study on the effect of alkali on the oxidation of sodium sulphite with air.[2]

Experimental. The experimental procedure was quite the same with that described in the previous paper. Air was passed at constant velocity into the mixture of stannous chloride and sodium hydroxide solution. The total volume of the mixture was made to 40 c.c. in each case. A part o sodium hydroxide is used for the precipitation of stannous hydroxide, and the excess of alkali was given as C_{NaOH} in the following tables. After t-minutes the air current was stopped and the total amount of the mixture, acidified with hydrochloric acid, was poured into a known quantity of

(1) *J. Am. Chem. Soc.*, **23** (1901), 119 and 450.
(2) Miyamoto, This Journal, **2** (1927), 74.

iodine solution and the excess of iodine was titrated back with sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the amount of stannous chloride; k was calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$, and $v_{calc.}$ was obtained by $v_{calc.}=v_0-kt$, using the mean value of k.

Table 1 shows that the oxidation velocity is independent of the amount of stannous hydroxide. When the concentration of alkali is less than about

TABLE 1.

Temp. = 20°C. Velocity of air = 7.78 litres per hour.

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0217	0	12.08	—	—
	20	10.90	11.02	0.0590
	25	10.69	10.75	0.0556
	30	10.52	10.49	0.0520
	35	10.20	10.22	0.0537
	0	8.37	—	—
	20	7.37	7.31	0.0500
	30	6.85	6.78	0.0507
	0	5.61	—	—
	20	4.55	4.55	0.0530
	30	4.09	4.02	0.0507
			Mean:	0.0531
0.1081	0	11.94	—	—
	9	9.82	9.87	0.236
	12	9.19	9.18	0.229
	15	8.59	8.49	0.223
	20	7.40	7.34	0.227
	30	4.98	5.04	0.232
	0	6.23	—	—
	12	3.45	3.47	0.232
	17	2.33	2.33	0.229
			Mean:	0.230

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.5500	0	11.43	—	—
	10	9.13	9.28	0.230
	12	8.86	8.85	0.214
	15	8.29	8.20	0.209
	20	7.40	7.13	0.202
	30	4.61	4.98	0.227
	0	23.14	—	—
	20	18.42	18.84	0.236
	30	17.00	16.69	0.205
	0	7.57	—	—
	10	5.48	5.42	0.209
	15	4.46	4.34	0.207
			Mean:	0.215

0.2 normal in the given condition, the mixture contains white precipitates of stannous hydroxide, and the phenomenon can be explained by considering that the oxidation takes place only in the liquid phase. But in more concentrated alkaline solutions all the precipitates dissolve, forming stannites, and it should be explained as in the case of sodium sulphite.[1]

The Effect of Sodium Hydroxide. The measurements were carried out in alkaline solutions of various concentrations, and the results are given in Table 2 and Fig. 1. The oxidation velocity of stannous hydroxide with air

TABLE 2.

Temp. = 20°C. Velocity of air = 7.78 litres per hour.

C_{NaOH} Normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.00595	0	11.39	—	—
	40	10.47	10.49	0.0230
	50	10.26	10.27	0.0226
	60	10.06	10.05	0.0222
	70	9.87	9.82	0.0217
			Mean:	0.0224
0.0217	See Table 1.			0.0531
0.04057	0	12.22	—	—
	20	10.32	10.43	0.0950
	25	10.13	9.99	0.0836
	30	9.53	9.54	0.0897
	35	9.11	9.09	0.0889
			Mean:	0.0893
0.1081	See Table 1.			0.230
0.1706	0	11.95	—	—
	10	9.19	9.38	0.276
	15	8.17	8.09	0.252
	20	6.88	6.81	0.254
	25	5.50	5.52	0.258
	30	4.57	4.24	0.246
			Mean:	0.257
0.2204	0	12.32	—	—
	9	9.88	9.99	0.271
	12	9.20	9.21	0.260
	14	8.85	8.69	0.256
	20	7.24	7.14	0.254
	24	6.24	6.10	0.253
			Mean:	0.259

C_{NaOH} Norma	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.3252	0	12.18	—	—
	9	9.80	9.97	0.264
	12	9.20	9.23	0.248
	15	8.54	8.49	0.243
	20	7.40	7.26	0.239
	25	6.33	6,03	0.234
			Mean:	0.246
0.5500	See Table 1.			0.215
1.130	0	12.65	—	—
	10	10.90	10.97	0.175
	12	10.68	10.63	0.164
	15	10.10	10.13	0.170
	20	9.29	9.29	0.168
	30	7.77	7.61	0.163
			Mean:	0.168
1.704	0	12.02	—	—
	20	9.32	9.50	0.135
	25	8.87	8.87	0.126
	30	8.36	8.24	0.122
	36	7.69	7.48	0.120
			Mean:	0.126
2.312	0	7.53	—	—
	10	6.49	6.53	0.104
	12	6.37	6.33	0.0967
	15	5.92	6.03	0.107
	20	5.63	5.53	0.0950
	27	4.93	4.84	0.0963
			Mean:	0.0998

(1) Previous paper.

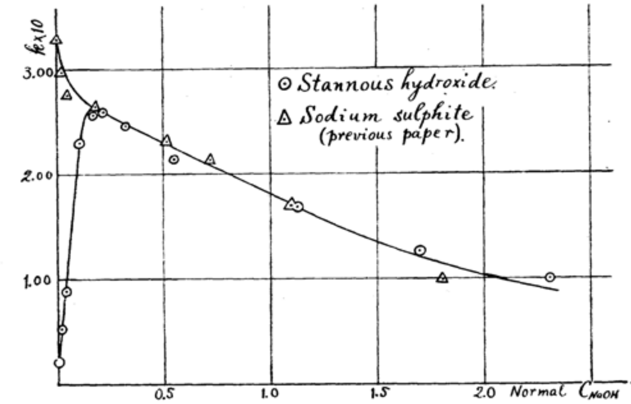

Fig. 1.

increases rapidly with the increase of the concentration of alkali until it attains a certain value and then decreases slowly. It was observed that the mixture contains white precipitates until the oxidation velocity attains almost its maximum value. In more concentrated alkaline solutions, all the stannous hydroxide dissolves forming stannites and the oxidation velocity was found to be the same as that of sodium sulphite. The results can be explained as follows.

The oxidation velocity increases until it attains the dissolution velocity of air with the increase of the concentration of alkali, which causes the formation of stannites. When the concentration of alkali increases still more, the dissolution velocity of air decreases, and consequently the oxidation velocity decreases. This assumption, which was also employed for the explanation of the oxidation velocity of sodium sulphite, was ascertained by the coincidence of their velocity constants as shown in Fig. 1. The values thus obtained can be regarded as the dissolution velocity of oxygen, when air was passed into 40 c.c. of solution in a test tube (diameter 3 cm.) through a glass tube (inside diameter = 4 mm. outside diameter = 6 mm.) at the rate of 7.78 litres per hour. From Fig. 1 we can calculate the approximate values of dissolution velocity of oxygen under the condition above described. Thus,

C_{NaOH} Normal	k	Dissolution velocity of oxygen
0.50	0.230	5.7×10^{-6} mols per minute.
1.00	0.180	4.5×10^{-6}
1.50	0.136	3.4×10^{-6}

The Effect of Temperature. The oxidation velocities at 30°C. and 40°C. are given in Table 3. The effect of temperature was small.

TABLE 3.

Velocity of air = 7.78 litres per hour.

Temp.	C_{NaOH} Normal	min.	v c.c.	$v_{calc.}$ c.c.	k
30°C.	0.0217	0	11.57	—	—
		30	8.99	9.16	0.0860
		35	8.76	8.76	0.0803
		40	8.56	8.36	0.0753
		50	7.61	7.56	0.0792
				Mean:	0.0802
30°C.	0.5500	0	11.14	—	—
		12	8.22	8.26	0.243
		15	7.44	7.54	0.247
		20	6.40	6.34	0.237
		25	5.32	5.14	0.233
				Mean:	0.240
40°	0.0217	0	10.35	—	—
		15	8.82	8.88	0.1020
		20	8.41	8.39	0.0970
		25	7.86	7.90	0.0996
		40	6.65	6.44	0.0925
				Mean:	0.0978
40°C.	0.5500	0	12.02	—	—
		10	9.17	9.22	0.285
		15	7.81	7.82	0.281
		20	6.50	6.42	0.276
		25	5.07	5.02	0.278
				Mean:	0.280

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.0802}{0.0531}=1.51 \quad \frac{k_{40^\circ}}{k_{30^\circ}}=\frac{0.0978}{0.0802}=1.22 \quad \text{When } C_{NaOH}=0.0217 \text{ normal}$$

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.240}{0.215}=1.12 \quad \frac{k_{40^\circ}}{k_{30^\circ}}=\frac{0.280}{0.240}=1.17 \quad \text{When } C_{NaOH}=0.5500 \text{ normal}$$

The Effect of the Velocity of Air Passed. It will be seen from Table 4 that a small change of the velocity of air current has not much influence on the oxidation velocity.

TABLE 4.

Temp. = 20°C. C_{NaOH} = 0.5500 Normal.

Velocity of air litres/hour	t min.	v c.c.	$v_{calc.}$ c.c.	k
6.67	0	11.31	—	—
	15	8.13	8.26	0.212
	20	7.11	7.25	0.210
	25	6.43	6.23	0.195
	30	5.35	5.22	0.199
			Mean:	0.203
10.00	0	11.81	—	—
	9	9.65	9.70	0.240
	15	8.35	8.30	0.231
	20	7.19	7.13	0.231
	25	5.96	5.96	0.234
			Mean:	0.234

Summary.

(1) The oxidation velocity of stannous chloride in alkaline solutions with air was studied. It was found to be the same as that of sodium sulphite when the concentration of alkali is greater than about 0.2 normal under the given condition.

(2) The effect of temperature was small.

(3) The dissolution velocity of oxygen in alkaline solutions was calculated indirectly.

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