THE EFFECT OF ALKALI ON THE OXIDATION OF SODIUM SULPHITE WITH AIR.

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It was described in the previous paper(1) that C. C. Palit and N. R. Dhar found(2) that some carbohydrates are oxidized with air in the presence of sodium sulphite and that the oxidation is accelerated on adding caustic alkali. They further measured the amount of sodium sulphite oxidized with air in the presence of carbohydrates and found that on adding caustic alkali the velocity of the oxidation of sodium sulphite decreases.(3) But it is not clear whether the retardation is the effect of the induced reaction or caustic alkali.

S. L. Bigelow(4) studied the catalytic action of many substances on the oxidation velocity of sodium sulphite with air, but the effect of alkali was not studied well. A. Titoff(5) studied the same phenomena also. In his experiment the oxidation was carried out in water which had been previously saturated with oxygen, that is, he studied the oxidation as a homogeneous reaction.

The purpose of this study is to know the effect of alkali more precisely by a modified method, and to discuss the promoting action of alkali on the induced oxidation, found by Dhar and Palit.

Experimental. The experimental procedure was quite the same with that described in the previous paper, only a large test-tube (diameter, 3 cm.) was used instead of an Erlenmeyer flask (100 c.c.), which was used in the previous experiment, for the vessel in which the oxidation takes place. Air, washed by acidified potassium dichromate solution and alkali, was passed at constant velocity into the solution of sodium sulphite of known concentration. The total volume of the solution was made to 40 c.c. in each case. After t minutes the air current was stopped and the total amount of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back by means of sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.09962 normal which is equivalent to the

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(1) S. Miyamoto, This journal, 2 (1927), 40

(2) Palit and Dhar, *J. Phys. Chem.*, 29 (1925), 799; 30 (1926), 939.

(3) *J. Phys. Chem.*, 30 (1926), 948.

(4) Bigelow, *Z. physik. Chem.*, 26 (1898), 493.

(5) Titoff, *Z. physik. Chem.*, 45 (1903), 641.

amount of sodium sulphite; k is calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$, and $v_{calc.}$ is obtained by $v_{calc.}=v_0-kt$, using the mean value of k.

TABLE 1.

Temp: 20°C. Air: 7.78 litres per hour. $C_{NaOH}=0$.

t min.	v c.c.	$v_{calc.}$ c.c.	k
0	16.71	—	—
10	13.42	13.41	0.329
15	11.87	11.76	0.322
20	10.03	10.11	0.334
30	7.40	6.81	0.310
0	29.16	—	—
8	26.48	26.52	0.335
10	25.75	25.86	0.341
12	25.12	25.20	0.337
15	24.05	24.21	0.341
24	21.49	21.24	0.320
0	38.64	—	—
9	35.73	35.67	0.323
12	34.54	34.68	0.342
22	31.56	31.38	0.322
		Mean:	0.330

Table 1 shows that the amount of sodium sulphite oxidized with air is independent of its concentration. This fact coincides with that obtained by Bigelow,(1) and can be explained by assuming that the velocity of the dissolution of oxygen into the solution is much slower than that of the oxidation of sodium sulphite.

The Effect of Alkali. The oxidation in sodium hydroxide solution of various concentrations was measured. The results are shown in Table 2.

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(1) Bigelow, *Z. physik. Chem.*, **26** (1898), 518.

TABLE 2.

Temp: 20°C. Air: 7.78 litres per hour.

C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k	C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
	0	13.23	—	—		0	14.25	—	—
0.02888	9	10.52	10.55	0.301	0.7219	8	12.57	12.55	0.210
	15	8.87	8.76	0.297		12	11.68	11.69	0.214
	25	5.63	5.78	0.304		14	11.30	11.27	0.210
	30	4.23	4.29	0.300		16	10.66	10.84	0.224
	35	3.20	2.80	0.287		25	9.10	8.92	0.206
			Mean	0.298				Mean	0.213
	0	12.05	—	—		0	12.37	—	—
0.05173	9	9.41	9.57	0.293	1.1011	9	10.77	10.85	0.178
	12	8.71	8.74	0.278		12	10.26	10.34	0.176
	15	7.95	7.91	0.273		15	9.86	9.83	0.167
	20	6.60	6.53	0.273		20	9.12	8.99	0.163
	30	4.11	3.77	0.265		30	7.52	7.30	0.162
			Mean	0.276				Mean	0.169
	0	12.18	—	—		0	12.17	—	—
0.1810	9	9.70	9.79	0.276	1.810	9	11.26	11.28	0.1011
	12	8.90	9.00	0.273		12	11.01	11.00	0.0967
	15	8.35	8.20	0.255		15	10.59	10.69	0.1053
	20	6.88	6.88	0.265		20	10.24	10.19	0.0965
	30	4.50	4.23	0.256		30	9.32	9.20	0.0950
			Mean	0.265				Mean	0.0989
	0	13.98	—	—					
0.5173	10	11.66	11.67	0.232					
	12	11.10	11.21	0.240					
	15	10.42	10.51	0.237					
	20	9.56	9.36	0.221					
	30	7.29	7.05	0.223					
			Mean	0.231					

Thus the sodium hydroxide diminishes the oxidation velocity of sodium sulphite. This will be explained by assuming the caustic alkali diminishes the dissolution velocity of oxygen into the solution. This assumption will also explain why the oxidation velocity of ferrous hydroxide(1) with air decreases with the increase of the concentration of caustic alkali, although its reducing power increases. Anyhow the increase of the induced oxidation of carbohydrates in the presence of sodium sulphite on adding caustic alkali is not due to the increase of the velocity of the primary reaction. Sodium

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(1) S. Miyamoto, This journal, 2 (1927), 40.

hydroxide can be regarded as one of the substances which accelerate the induced reaction but not the primary reaction. The mechanism of this kind of promoters of induced reaction can be explained by the theory of the transference of active states.(1)

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are shown in Table 3. The effect of temperature was very small.

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.345}{0.330}=1.05,\quad \frac{k_{40^\circ}}{k_{39^\circ}}=\frac{0.382}{0.345}=1.11 \quad \text{when } C_{\mathrm{NaOH}}=0$$

$$\frac{k_{30^\circ}}{k_{20^\circ}}=\frac{0.265}{0.231}=1.15,\quad \frac{k_{40^\circ}}{k_{30^\circ}}=\frac{0.301}{0.265}=1.14 \quad \text{when } C_{\mathrm{NaOH}}=0.5173 \text{ Normal}$$

TABLE 3.

Air: 7.78 litres per hour.

Temp. C.	C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30°C	0	0	13.69	—	—
		9	10.52	10.58	0.352
		12	9.37	9.55	0.360
		15	8.50	8.51	0.346
		20	7.00	6.79	0.335
		30	3.78	3.11	0.330
					Mean 0.345
30°	0.5173	0	13.69	—	—
		9	11.18	11.30	0.279
		12	10.57	10.51	0.260
		15	9.73	9.71	0.264
		20	8.42	8.39	0.264
		30	6.01	5.74	0.256
					Mean 0.265
40°	0	0	11.84	—	—
		9	8.24	8.40	0.400
		12	7.35	7.26	0.374
		15	5.82	6.11	0.401
		20	4.52	4.20	0.366
		25	2.61	2.29	0.369
					Mean 0.382
40°	0.5173	0	11.41	—	—
		9	8.62	8.70	0.310
		12	7.64	7.80	0.314
		15	7.07	6.89	0.289
		20	5.07	5.39	0.311
		30	3.00	2.38	0.280
					Mean 0.301

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(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 257.

The Effect of the Velocity of Air Passed. Table 4 is the results measured when air was passed at the rate of 6.67 and 10 litres per hour. By comparing this with Table 1, it will be seen that the oxidation velocity increases with the increase of the velocity of air current passed.

TABLE 4.

Temp: 20°C. $C_{NaOH}=0$.

Air litres per hour	t min.	v c.c.	$v_{calc.}$ c.c.	k
	0	13.57	—	—
6.67	9	10.87	10.87	0.300
	12	9.84	9.97	0.311
	15	9.20	9.07	0.291
	20	7.18	7.57	0.313
	30	5.00	4.57	0.286
			Mean	0.300
	0	12.98	—	—
10.0	9	9.68	9.79	0.367
	12	8.65	8.73	0.361
	15	7.70	7.67	0.352
	20	5.98	5.90	0.350
	30	2.75	2.36	0.341
			Mean	0.354

Summary.

1. The oxidation velocity of sodium sulphite with air was independent of its concentration.
2. Caustic alkali diminishes the velocity of the oxidation.
3. The effect of temperature was small.

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