ON THE OXIDATION OF THE MIXTURE OF STANNOUS HYDROXIDE AND SODIUM SULPHITE IN SODIUM CARBONATE SOLUTION WITH AIR.

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Introduction. It was observed that the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide solution oxidizes very slowly first with air, when the initial concentration of stannous hydroxide is small.(1) The author has an opinion to explain the fact by the transference of active states.(2) If we accept the idea that the active states of the molecules of sodium sulphite transfers to the molecules of stannous hydroxide, it is easy to explain the experimental results as follows.

When the concentration of stannous hydroxide is very small, the oxidation velocity of the mixture with air should be very small first, for stannous hydroxide oxidizes alone, if the active states of the molecules of sodium sulphite transfer to the molecules of stannous hydroxide. After the disappearance of the molecules of stannous hydroxide by the oxidation, sodium sulphite begins to oxidize and the oxidation velocity of the mixture increases. Thus the oxidation of the mixture in sodium hydroxide solution, which will be regarded as a kind of negative induced reaction, can be explained by the transference of active states.

According to this idea, the mixture of sodium sulphite and stannous hydroxide in sodium carbonate solution, should oxidize very slowly, for the oxidation velocity of stannous hydroxide in sodium carbonate solution(3) is very small, though sodium sulphite oxidizes quickly, if it be alone.(4) The present reseach was carred out to ascertain this idea.

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(1) S. Miyamoto, this journal, 2 (1927), 196.

(2) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research,* 4 (1926), 259

(3) S. Miyamoto, this journal, 3 (1928), 43.

(4) S. Miyamoto, ibid., 3 (1928), 76.

Experimental: The experimental procedure was quite the same as that employed in the previous study on the oxidation of the mixture in sodium hydroxide solution.⑴ In the following Tables, v is the volume of sodium thiosulphate solution of 0.0996 normal which is equivalent to the total amount of sodium sulphite and stannous chloride, $v_{0}(\mathrm{SnCl_2})$ and $v_{0}(\mathrm{Na_2SO_3})$ being the initial amounts of stannous chloride and sodium sulphite respectively.

If the oxidation of stannous hydroxide take place alone, v should have the value v' given in the following tables, which was calculated by $v' = v_0 - k't$, k' being the velocity constant of the oxidation of stannous hydroxide in sodium carbonate solution given in the previous paper.

If sodium sulphite oxidize alone, v should have the value v'' given in the following tables, which was calculated by $v'' = v_0 - k''t$, k'' being the velocity constant of the oxidation of sodium sulphite and calculated by $k = 0.258-0.114\ C_{\mathrm{Na_2CO_3}}$, given in the previous paper.

TABLE 1.

Temp.=20°C. $C_{\mathrm{Na_2CO_3}}$=0.2780 normal.
Velocity of air=7.78 litres per hour.

$v_0(\mathrm{SnCl_2})$ c.c.	$v_0(\mathrm{Na_2SO_3})$ c.c.	t min.	v c.c.	v' c.c.	v'' c.c.
12.98	2.89	0	15.87	—	—
		15	15.73	15.77	—
		30	15.70	15.66	—
		60	15.62	15.46	—
8.14	11.32	0	19.46	—	—
		10	19.30	19.39	17.20
		30	19.19	19.25	12.68
		60	19.05	19.05	5.90
1.69	19.82	0	21.51	—	—
		10	21.39	21.44	19.25
		40	21.09	21.23	12.47
		60	21.03	21.10	7.95
0.42	13.72	0	14.14	—	—
		10	13.95	—	11.88
		30	13.75	—	7.36
		60	13.47	—	0.58
0.13	20.48	0	20.61	—	—
		10	20.06	—	18.35
		50	20.03	—	9.31
0.031	15.33	0	15.36	—	—
		10	15.20	—	13.10
		30	10.95	—	8.57
		60	5.46	—	1.80

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(1) Loc. cit.

TABLE 2.

Temp. = 20°C. $C_{Na_2CO_3} = 0.4655$ normal.
Velocity of air = 7.78 litres per hour.

$v_0(SnCl_2)$ c.c.	$v_0(Na_2SO_3)$ c.c.	t min.	v c.c.	v' c.c.	v'' c.c.
16.74	1.21	0	17.95	—	—
		10	17.90	17.88	—
		30	17.80	17.74	—
		60	17.68	17.54	—
7.93	10.71	0	18.64	—	—
		10	18.56	18.57	16.59
		30	18.40	18.43	12.49
		60	18.29	18.23	6.34
1.66	13.71	0	15.37	—	—
		15	15.19	15.27	12.29
		35	14.99	15.13	8.19
		60	14.85	14.96	3.07
0.44	18.25	0	18.69	—	—
		10	18.48	—	16.64
		60	18.20	—	6.39
0.12	16.37	0	16.49	—	—
		10	16.17	—	14.44
		30	15.85	—	10.34
		60	15.78	—	4.19
0.024	16.22	0	16.24	—	—
		8	16.15	—	14.60
		25	12.75	—	11.11
		50	8.29	—	5.99

It seems from Table 1 and 2, that stannous hydroxide alone is oxidized, when air is passed into the mixture in sodium carbonate solution, as is expected. When the initial concentration of stannous hydroxide is very small, the mixture is oxidized very slowly first and increases afterwards, as is shown in the Tables. The result is easily explained quite the same way as in the case of the oxidation of the mixture in sodium hydroxide solution, by accepting the idea above described.

Thus the oxidation of the mixture of stannous hydroxide and sodium sulphite is an example of negative induced reaction ; the oxidation of the first substance has an inhibiting action on the oxidation of the second one. The mechanism of the reaction can be explained by the transference of active states.(1)

Summary.

1. The oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium carbonate solution was studied.

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(1) Loc. cit.

2. It was observed that the reaction is an example of negative induced reaction; the oxidation of stannous hydroxide has an inhibiting action on the oxidation of sodium sulphite.
3. The mechanism of the reaction was discussed.

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