ON THE OXIDATION OF SODIUM SULPHITE BY AIR IN THE PRESENCE OF FERROUS HYDROXIDE AND A THEORY OF NEGATIVE INDUCED REACTION.

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Introduction. The present research was undertaken with an expectation that the oxidation of the mixture of sodium sulphite and ferrous hydroxide in sodium hydroxide solution in a vessel will be an example of negative induced reaction favourable to the author's theory,(1) in connection with the former study on the oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide(2) solution or in sodium carbonate(3) solution by air, which was found to be a kind of negative induced reaction.

A Theory of Negative Induced Reaction. When two independent chemical reactions take place simultaneously in a same vessel, sometimes the primary reaction has an accelerating or an inhibiting action on the secondary reaction. In the former case, the phenomenon is usually called induced reaction, and in the latter case, it will be probable to be called negative induced reaction.

According to the modern theory of the kinetics of chemical reaction, the velocity of a reaction is accelerated by the appropriate activation of the molecules of the reacting substances. It is then quite probable to consider

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(1) S. Miyamoto, *Sci. Papers Inst. Phys. Chem. Research*, **4** (1926), 259.

(2) S. Miyamoto, this Bulletin, **2** (1927), 191; *Sci. Papers Inst. Phys. Chem. Research*, **7** (1927), 195.

(3) S. Miyamoto, this Bulletin, **3** (1928), 95; *Sci. Papers Inst. Phys. Chem. Research*, **8** (1928), 237.

that the phenomenon, called induced reaction, is no other than the activating action of the primary reaction, which can proceed by itself, on the molecules of the reacting substances of the secondary reaction, whose own reaction velocity is extremely small.

Various kinds of possible activating processes can be considered. It was proposed by the author,(1) that the direct transference of the appropriate active states of the reaction products of the primary reaction to the molecules of the reacting substances of the secondary reaction can be regarded as one of the possible processes of activation at least for some induced reactions.

The phenomenon, called negative induced reaction, can be considered to be the reverse process. In this case, the active states of the molecules of the reacting substances of the secondary reaction, already activated, lose their activity, before they react each other, by some means in the presence of the primary reaction.

The direct transference of active states will also be one of the possible mechanisms for this phenomenon. According to this consideration, the existence of three kinds of negative induced reactions can be considered. The active states of the molecules of the reacting substances of the secondary reaction can transfer firstly to the molecules of the reacting substances, secondly to the molecules of the reaction products and thirdly to the molecules of both of the reacting substances and reaction products of the primary reaction. It should be considered that the direct transference of active states depends upon the mutual specific nature of the colliding molecules. Then the negative induced reaction of the third kind will scarcely occur in the actual case.

In the case of the negative induced reaction of the first kind, the velocity of the secondary reaction will be very small at the beginning, and increase with time as the concentration of the reacting substances of the primary reaction decreases.

In the case of the negative induced reaction of the second kind, the velocity of the secondary reaction will not be small at the beginning, but decreases with time as the concentration of the reaction products of the primary reaction increases. Then in this case, the phenomenon can be regarded as the negative catalytic action of some of the reaction products of the primary reaction, whose concentrations increase with time.

The oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide(2) or in sodium carbonate(3) solution by means of air was

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(1) S. Miyamoto, *Sci. Papers Inst. Phys. Chem. Research*, **4** (1926), 259.

(2) Loc. cit.

(3) Loc. cit.

found to be an example of negative induced reaction of the first kind. The inhibiting action of the oxidation of stannous hydroxide on the oxidation of sodium sulphite, and the increase of the oxidation velocity of the mixture in sodium hydroxide solution with the suitable elapse of time, when the initial concentration of stannous hydroxide is small, are the principal evidences that it is the negative induced reaction of the second kind.

With the expectation that the oxidation of the mixture of sodium sulphite and ferrous hydroxide in sodium hydroxide solution by means of air will also be the same kind of phenomenon, the present research was undertaken. Favourable result to the author's theory, above described, was obtained. The oxidation velocity of the mixture was found to be an example of negative induced reaction of the second kind.

The oxidation velocity of ferrous hydroxide(1) or sodium sulphite(2) in sodium hydroxide solution by means of air was already studied under certain conditions. They are considerably great and the observed oxidation velocity of each shows the dissolution velocity of oxygen into the solution. In the present research, the mixture was treated under the same conditions, and the rate of the oxidation of sodium sulphite alone was observed. The experimental results, which will be given in the later, show that it is a negative induced reaction of the second kind, the oxidation of ferrous hydroxide and that of sodium sulphite being considered as the primary and the secondary reactions respectively. It was unnecessary for the present purpose to observe the oxidation velocity of ferrous hydroxide in the mixture, which will be expressed by

(The oxidation velocity of $Fe(OH)_2$ in the mixture) $\leq$
(The dissolution velocity of oxygen)—(The oxidation velocity of Na_2SO_3 in the mixture).

Experimental.

The experimental procedure was almost the same as that employed in the previous studies.(3)

A large test tube (diameter ≒ 3 cm.) was used for the reacting vessel, the total volume of the mixture being made to 40 c.c. in each case. After t—minutes, the air current, which was passed into the mixture through a glass tube (inside diameter ≒ 4 mm., outside diameter ≒ 6 mm.) after being washed by acidic solution of potassium bichromate and sodium hydroxide

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(1) S. Miyamoto, this Bulletin, **3** (1928), 137; *Sci. Papers Inst. Phys. Chem. Research*, **9** (1928), 203.

(2) S. Miyamoto, this Bulletin, **2** (1927), 74; *Sci. Papers Inst. Phys. Chem. Research*, **7** (1927), 40.

(3) Loc. cit.

solution, was stopped, and the total amount of the mixture was quickly filtered and washed under reduced pressure into a known amount of iodine solution, acidified with hydrochloric acid. 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 0.0996 normal, equivalent to the quantity of sodium sulphite, remained in the mixture after the t—minutes passage of air. The amount of ferrous hydroxide, initially present in the mixture, was determined separately by the titration by means of 0.1000 normal solution of potassium permanganate, the values of $v_{0\,\mathrm{Fe(OH)_2}}$ in the following tables being the volume of potassium permanganate solution, equivalent to the amount of ferrous hydroxide, present in the mixture at $t=0$.

Thus the oxidation velocity of sodium sulphite in the mixture was only observed. The results were quite sufficient for the present purpose, above descrived.

Table 1.

Temp. $=20°$C. $C_{\mathrm{NaOH}}=0.2000$ normal

Air $=7.78$ litres per hour.

$v_{0\,\mathrm{Fe(OH)_2}}$ c.c.	t min.	$v_{(\mathrm{Na_2SO_3})}$ c.c.	$v'_{(\mathrm{Na_2SO_3})}(=v_0-0.260\,t)$ c.c.
10.90	0	13.69	—
	10	12.41	11.09
	30	12.21	5.89
	120	12.02	—
9.20	0	13.90	—
	10	12.94	11.30
	30	12.47	6.10
	120	12.13	—
9.20	0	13.46	—
	10	12.55	10.86
	30	12.23	5.66
	120	12.08	—
5.45	0	9.53	—
	10	8.48	6.93
	30	8.25	1.73
	120	8.09	—
5.45	0	18.71	—
	10	17.35	16.11
	30	17.22	10.91
	120	16.78	—

Table 1. *(continued)*

$v_{0\,\mathrm{Fe(OH)_2}}$ c.c.	t min.	$v_{(\mathrm{Na_2SO_3})}$ c.c.	$v'_{(\mathrm{Na_2SO_3})}(=v_0-0.260\,t)$ c.c.
2.30	0	13.15	—
	10	11.83	10.55
	25	11.55	6.65
	50	11.50	0.15
2.30	0	22.00	—
	10	21.18	19.40
	25	21.00	15.50
	120	20.06	—
2.30	0	13.37	—
	10	12.26	10.77
	25	12.11	6.87
	120	11.79	—
0.109	0	12.59	—
	10	9.90	9.99
	30	8.62	4.79
	120	7.37	—
0.058	0	10.35	—
	10	8.16	7.75
	25	7.12	3.85
	120	5.73	—
0.044	0	14.11	—
	10	11.54	11.51
	30	9.71	6.31
	120	7.82	—
0.022	0	12.46	—
	10	9.87	9.86
	30	7.80	4.66
	120	6.33	—

Table 2.

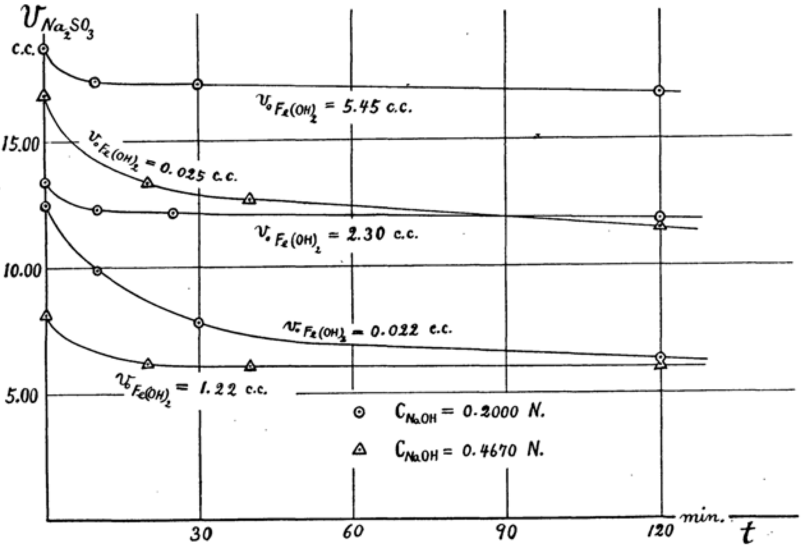
Temp. = 20°C. $C_{\mathrm{NaOH}}=0.4670$ normal.

Air = 7.78 litres per hour.

$v_{0\,\mathrm{Fe(OH)_2}}$ c.c.	t min.	$v_{(\mathrm{Na_2SO_3})}$ c.c.	$v'_{(\mathrm{Na_2SO_3})}=(v_0-0.234\,t)$ c.c.
12.23	0	12.96	—
	20	11.80	8.28
	40	11.72	3.60
	120	11.63	—
6.12	0	18.84	—
	21	17.02	13.93
	40	16.85	9.48
	120	16.77	—

Table 2. *(continued)*

$v_{0\,\mathrm{Fe(OH)_2}}$ c.c.	t min.	$v_{(\mathrm{Na_2SO_3})}$ c.c.	$v' = (v_0 - 0.234\,t)$ $(\mathrm{Na_2SO_3})$ c.c.
2.45	0	20.69	—
	20	19.18	16.01
	40	19.03	11.33
	120	18.68	—
1.22	0	8.13	—
	20	6.19	3.45
	40	6.09	—
	120	6.05	—
0.122	0	10.44	—
	20	6.47	5.76
	40	5.42	1.08
	120	4.87	—
0.050	0	14.70	—
	20	10.42	10.02
	40	8.74	5.34
	120	7.42	—
0.025	0	16.81	—
	20	13.32	12.13
	40	12.63	7.45
	120	11.46	—



As is shown in Table 1 and 2, the oxidation velocity of sodium sulphite in the presence of ferrous hydroxide by means of air decreases rapidly with time; a few of the results being graphically shown in the accompanying figure. The values of v', given in the last column of the tables are calculated by an equation,

$$v' = v_0 - kt,$$

k being the velocity constant of the oxidation of sodium sulphite⁽¹⁾ in the absence of ferrous hydroxide, obtained in the previous study. When the initial concentration of ferrous hydroxide is very small, the values of v and v' are almost the same at the beginning; that is, sodium hydroxide oxidizes in the first stage almost at the same velocity as it is oxidized alone, but the velocity decreases gradually with time. It is not diminished so rapidly as in the other cases, since ferric hydroxide is formed at a very slow rate, when the initial concentration of ferrous hydroxide is very small.

The experimental results show that it is an example of negative induced reaction of the second kind, and the direct transference of the active states of the molecules of sodium sulphite to the molecules of ferric hydroxide, the reaction product of the primary reaction, will be one of the proper interpretations for this phenomenon.

The Effect of Ferric Hydroxide. The observed results on the oxidation of the mixture, an example of negative induced reaction of the second kind, should be considered to be the negative catalytic action of ferric hydroxide, according to the theory, above described. To ascertain this consideration, the oxidation velocity of sodium sulphite in the presence of ferric hydroxide was studied under the same conditions, quite the same way as was above described. The amount of ferric hydroxide was determined by the usual method of iodometry, the value of $v_{0\,Fe(OH)_3}$ in Table 3 and 4 being the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the amount of ferric hydroxide, present in the reacting mixture.

Table 3.

Temp. = 20°C. $C_{NaOH} = 0.2000$ normal.

Air = 7.78 litres per hour.

$v_{0\,Fe(OH)_3}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v'(=v_0)-0.260\,t)$ (Na_2SO_3) c.c.
10.65	0	12.86	—
	10	12.59	10.26
	30	12.50	5.06
	120	12.35	—

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(1) Loc. cit.

Table 3. *(continued)*

v_0 $Fe(OH)_3$ c.c.	t min.	v (Na_2SO_3) c.c.	$v'(=v_0-0.260\,t)$ (Na_2SO_3) c.c.
4.26	0	13.77	—
	10	13.44	11.17
	30	13.31	5.97
	120	13.27	—
2.13	0	19.01	—
	10	18.48	16.41
	30	18.40	11.21
	120	18.33	—
2.13	0	17.43	—
	10	16.94	14.83
	30	16.73	9.63
	120	16.72	—
2.13	0	9.32	—
	10	8.82	6.72
	30	8.75	1.52
	120	8.73	—
0.213	0	18.45	—
	10	17.86	15.85
	30	17.37	10.65
	120	17.12	—
0.210	0	10.90	—
	10	10.53	8.30
	30	10.17	3.10
	120	9.87	—
0.085	0	15.85	—
	10	15.13	13.25
	30	14.89	8.05
	120	14.62	—
0.085	0	13.06	—
	10	12.34	10.46
	30	12.19	5.26
	120	12.06	—
0.043	0	13.50	—
	10	12.73	10.90
	30	12.46	5.70
	120	11.82	—
0.021	0	13.31	—
	10	12.13	10.71
	30	11.78	5.51
	120	11.49	—

Table 4.

Temp. = 20°C. C_{NaOH} = 0.4670 normal.

Air. = 7.78 litres per hour.

$v_{0\,Fe(OH)_3}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v'=(v_0-0.234\,t)_{(Na_2SO_3)}$ c.c.
13.20	0	16.92	—
	15	16.62	13.41
	45	16.58	6.39
	120	16.58	—
6.60	0	16.50	—
	20	16.29	11.82
	40	16.29	7.14
	120	16.25	—
2.64	0	15.90	—
	20	15.77	11.22
	40	15.70	6.54
	120	15.60	—
1.32	0	12.88	—
	20	12.84	8.20
	40	12.68	3.52
	120	12.66	—
0.65	0	11.70	—
	20	11.60	7.02
	40	11.57	2.34
	120	11.41	—
0.132	0	19.66	—
	20	19.46	14.98
	40	19.43	10.30
	120	19.27	—
0.053	0	10.00	—
	20	9.54	5.32
	40	9.41	0.64
	120	9.19	—
0.026	0	16.69	—
	20	15.88	12.01
	40	15.62	7.33
	120	15.36	—

As was shown in the Tables a favourable result to the author's considerations was obtained: the oxidation velocity of sodium sulphite in the presence of ferric hydroxide is very small.

The Effect of Sodium Sulphate. Though it is almost certain that sodium sulphate formed by the oxidation of sodium sulphite has a negligible effect on the oxidation velocity of sodium sulphite under the conditions of the author's measurements by the previous studies, it was ascertained by measuring the oxidation velocity in the presence of a considerable amount of sodium sulphate.

$v_{0\,Na_2SO_4}$ in Table 5 is the volume of 0.1000 normal solution of sodium sulphate initially present in the mixture.

Table 5.

Temp. = 20°C. $C_{NaOH} = 0.2000$ normal.

Air = 7.78 litres per hour.

$v_{0\,Fe(OH)_2}$ c.c.	$v_{0\,Fe(OH)_3}$ c.c.	$v_{0\,Na_2SO_4}$ c.c.	t min	v c.c.
2.30	—	10.00	0	12.77
			10	11.63
			25	11.52
			60	11.23
0.116	—	10.00	0	12.49
			11	10.16
			25	9.27
			120	7.86
—	0.085	10.00	0	14.79
			10	14.06
			30	13.63
			120	13.32

By comparing Table 5 and Table 1—4, it will be seen that sodium sulphate has no appreciable effect on the oxidation velocity of sodium sulphite.

The experimental error of the present measurements is considerably great owing to the slowness of the reaction velocity, and it will be of no use to try to obtain any quantitative relation from the values, given in the tables.

Summary.

1. A theory of negative induced reaction was proposed. Three kinds of negative induced reactions was considered according to the proposed theory. The oxidation of the mixture of stannous hydroxide and sodium sulphite in sodium hydroxide or in sodium carbonate solution by means of air, the results of which being already reported in the previous papers, can be regarded as an example of negative induced reaction of the first kind, and the oxidation of the mixture of ferrous hydroxide and sodium sulphite

in sodium hydroxide solution, here reported, as an example of negative induced reaction of the second kind.

2. The oxidation of the mixture of sodium sulphite and ferrous hydroxide in sodium hydroxide solution by means of air was studied, with an expectation, that it will give an example of negative induced reaction. The oxidation velocity of sodium sulphite in the mixture was only measured, which was sufficient for the present purpose. The velocity decreases rapidly with time, and the result was interpreted as a negative induced reaction of the second kind.

3. To ascertain that the decrease of the observed oxidation velocity of sodium sulphite in the mixture is due to the formation of ferric hydroxide, the reaction product of the primary reaction, the oxidation velocity of sodium sulphite in the presence of ferric hydroxide was studied under the same conditions. The expectation was fulfilled.

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