THE EFFECT OF ALKALI ON THE OXIDATION OF FERROUS HYDROXIDE WITH AIR.

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C. C. Palit and N. R. Dhar have found that some carbohydrates are oxydized by passing air through their solutions in the presence of ferrous hydroxide or sodium sulphite, and that the velocities of these induced oxidations increase with the increase of the concentration of caustic alkali almost in every case.(1) More or less similar results were obtained by Mittra and Dhar on the oxidation of nickelous hydroxide with air in the presence of ferrous hydroxide.(2) It may be supposed that the caustic alkali, which promotes the induced reaction is one of the substances which accelerate the primary reaction. In the case of ferrous hydroxide this expectation is more probable, for the reducing action of ferrous hydroxide increases as the concentration of alkali increases.(3) The present experiment has been

(1) Palit and Dhar, *J. Phys. Chem.*, **29** (1925), 799; **30** (1926). 939.
(2) Mittra and Dhar, *Z. anorg Chem.*, **122** (1922), 146.
(3) Miyamoto, *Japanese Journal of Chemistry*, **1** (1922), 57; *Scientific Papers of the Institute of Physical and Chemical Research*, **1** (1922), 31.

undertaken to know the effect of alkali on the primary reaction, for the purpose of knowing its effect on the induced reaction above described. From the result of the experiment, it has been ascertained that the caustic alkali does not promote the oxidation, but on the contrary, it decreases the velocity of oxidation. This is one of the examples which show the possibility of the existence of substances which do not promote the primary reaction but accelerate the induced reaction, and the mechanism of this phenomenon may be explained by the theory of the transference of active states.[1]

Experimental. A certain amount of ferrous sulphate solution of known concentration is added to a known quantity of sodium hydroxide solution of known concentration, and air, purified by passing through an acidic solution of potassium bichromate and sodium hydroxide solution, is passed at constant velocity into the mixture. The total volume of the mixture was made to 40 c.c. in each case. The concentration of sodium hydroxide given in the following tables are those calculated after the addition of ferrous sulphate solution. After t minutes the air current is stopped and the contents of the vessel are dissolved by adding sulphuric acid, and the ferrous sulphate thus formed is titrated with potassium permanganate solution (0.1018 normal), the volume of which is given as v in the following tables. The values of k in the following tables were obtained graphically, and those of $v_{calc.}$ were calculated by the equation, $v_{calc.}=v_0-kt$, v_0 being the value of v at $t=o$.

TABLE 1.

Temp. = 20°C. Velocity of air = 7.78 litres per hour. Concentration of alkali (C_{NaOH}) = 2.240 mol per litre. $k=0.140$ or $v_{calc.}=v_0-0.140\ t$.

t min.	v c.c.	$v_{calc.}$ c.c.	t min.	v c.c.	$v_{calc.}$ c.c.
0	9.11	—	0	12.60	—
6	8.10	8.27	6	11.50	11.76
8	8.00	7.99	8	11.32	11.48
10	7.74	7.71	10	11.18	11.20
12	7.54	7.43	12	10.97	10.92
15	7.05	7.01	15	10.66	10.50
0	10.83	—	0	18.20	—
6	9.90	9.99	6	17.11	17.36
8	9.65	9.71	8	16.99	17.08
10	9.30	9.43	10	16.69	16.80
12	9.20	9.15	12	16.51	16.52
15	8.79	8.73	15	16.12	16.10

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

From the above results we see that the velocity of oxidation of ferrous hydroxide with air is zero order with regard to the amount of ferrous hydroxide, or the amount of ferrous hydroxide oxidized is independent of the quantity of hydroxide present. This can be explained by considering that the oxidation takes place in the liquid phase and not on the surface of the solid phase, because in liquid phase the concentration of ferrous ion, although it is extremely small, will be constant during the process.

The Effect of Alkali. Table 2 shows the results of the measurements which were carried out in the sodium hydroxide solution of different concentrations. The values of k decrease with the increase of the concentration of the alkali.

TABLE 2.

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

C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.		C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.	
0.0048	0	9.11	—	$k=0.310$	0.870	0	9.06	—	$k=0.230$
	6	7.10	7.25			6	7.54	7.68	
	8	6.76	6.63			8	7.15	7.22	
	10	5.90	6.01			10	6.82	6.76	
	12	5.49	5.39			12	6.45	6.30	
	15	4.85	4.46			15	5.84	5.61	
0.0894	0	9.11	—	$k=0.300$	1.320	0	9.06	—	$k=0.203$
	6	7.15	7.31			6	7.66	7.84	
	8	6.60	6.71			8	7.28	7.44	
	10	5.96	6.11			10	7.10	7.03	
	12	5.61	5.51			12	6.69	6.62	
	15	4.85	4.61			15	6.20	6.01	
0.410	0	9.06	—	$k=0.278$	3.150	0	9.06	—	$k=0.110$
	6	7.20	7.39			6	8.25	8.40	
	8	6.65	6.84			8	8.07	8.18	
	10	6.41	6.28			10	7.97	7.96	
	12	5.65	5.72			12	7.76	7.74	
	15	5.06	4.89			15	7.58	7.41	

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are shown in Table 3. Thus the effect of temperature on the velocity of oxidation of ferrous hydroxide by the air is rather small.

TABLE 3.

Velocity of air = 7.78 litres per hour.

Temp. C°.	C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.		Temp. C°.	C_{NaOH} mol/litre	t min.	v c.c.	$v_{calc.}$ c.c.	
30	2.240	0	9.05	—		40	2.240	0	9.02	—	
		6	7.96	8.09				6	7.88	7.92	
		8	7.71	7.77	$k=0.160$			8	7.50	7.55	$k=0.184$
		10	7.39	7.45				10	7.22	7.18	
		12	7.17	7.13				12	6.91	6.81	
		15	6.75	6.65				15	6.40	6.26	
30	0.870	0	9.05	—		40	0.870	0	9.02	—	
		6	7.50	7.64				6	7.38	7.54	
		8	7.03	7.17	$k=0.235$			8	7.09	7.04	$k=0.247$
		10	6.85	6.70				10	6.64	6.55	
		12	6.32	6.23				12	6.09	6.06	
		15	5.73	5.52				15	5.53	5.32	

$$\frac{k_{30°}}{k_{20°}}=1.14 \quad \text{and} \quad \frac{k_{40°}}{k_{30°}}=1.15 \quad \text{when} \quad C_{NaOH}=2.240 \text{ mol/litre.}$$

$$\frac{k_{30°}}{k_{20°}}=1.02 \quad \text{and} \quad \frac{k_{40°}}{k_{30°}}=1.05 \quad \text{when} \quad C_{NaOH}=0.870 \text{ mol/litre.}$$

The Effect of the Velocity of Air Current Passed. In the measurements above described, air was passed at the rate of 7.78 litres per hour. Table 4 shows the results obtained when the velocity of air current was changed. By comparing these values with those given in Table 1, it will be seen that the velocity of the oxidation increases slightly with the increase of the velocity of air current.

TABLE 4.

Temp. = 20°C. C_{NaOH} = 2.240 mol per litre.

Velocity of air litre/hour	t min.	v c.c.	$v_{calc.}$ c.c.		Velocity of air litre/hour	t min.	v c.c.	$v_{calc.}$ c.c.	
6.67	0	8.95	—		10.00	0	8.90	—	
	6	8.07	8.19			6	7.90	8.02	
	8	8.02	7.94	$k=0.126$		8	7.75	7.73	$k=0.146$
	10	7.71	7.69			10	7.52	7.44	
	12	7.39	7.44			12	7.24	7.15	
	15	7.12	7.06			15	6.90	6.71	

Summary.

The velocity of the oxidation of ferrous hydroxide with air was found to be independent of the quantity of ferrous hydroxide in a definite volume.

The effect of temperature on the reaction was small.

Caustic alkali does not promote the oxidation, and on the contrary, it decreases the velocity of oxidation, notwithstanding the reducing power of ferrous hydroxide increases with the increase of the concentration of alkali. From this result, we may suppose that the increase of the velocity of oxidation of carbohydrates or nickelous hydroxide by the addition of caustic alkali is not due to the increase of the velocity of primary reaction.

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