THE FUSION OF SODIUM HYDROXIDE WITH SOME INORGANIC SALTS.

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In the course of an investigation initiated for quite another purpose, it became desirable to determine the nature of the action of fused sodium hydroxide upon sodium arsenite and other salts. The working hypothesis which had been devised by the senior author to assist in the main investigation, indicated the probability that in such fusion the elements of water are active, and that oxidations might be possible whose mechanism would consist of a decomposition of water, the oxygen being taken up by the sodium arsenite or other oxygen acceptor present, and the hydrogen evolved in the free state. Our experiments have confirmed this expectation. Sodium arsenite is oxidized to arsenate with the evolution of an equivalent amount of hydrogen. It seemed desirable to expand this investigation to other oxygen acceptors, with a view of determining to what extent this oxidizing action induced by sodium hydroxide is applicable. We have accordingly studied the action in the case of a number of inorganic salts, which might conceivably pass, under such conditions, from a lower to a higher stage of oxidation, and thus act as oxygen acceptors.

A search of the literature showed a few isolated cases recorded of such oxidations. Most of these are qualitative observations that oxidation has occurred, but without any quantitative observation regarding the change. To this class belong the observations of Peligot,[1] that chromous hydroxide mixed with aqueous potassium hydroxide is oxidized with the evolution of hydrogen, of Bloxam,[2] who states in his text book that hypophosphites when boiled with caustic alkalis are converted into phosphates with the evolution of hydrogen, of Baugé[3] that the compound $2Cr_3O_4.3H_2O$ has been obtained by the decomposition of potassium chromous carbonate by boiling water, with the evolution of hydrogen and carbon dioxide. Quantitative observations were made by Muthmann and Nagel[4] on the transformation of molybdenum dichloride into the trihydroxide with evolution of hydrogen, by boiling with potassium hydroxide solution.

None of these papers make any reference to the general nature of the reaction, or offer any explanation of its mechanism.

[1] *Ann. chim. phys.*, [3] **12**, 538 (1844).

[2] 10th Ed., p. 222.

[3] *Compt. rend.*, **127**, 551 (1898).

[4] *Ber.*, **31**, 2009 (1898).

TABLE I.—GAS ANALYTICAL RESULTS.

No.	Compounds.	Oxygen.			Hydrogen produced. Cc.	Nitrogen present. Cc.	Time of heating. Mins.	Temperature. Degrees.
		At start. Cc.	At end. Cc.	Used up. Cc.				
1	0.4000 g. sod. arsenite + 1 g. sodium hydroxide......	10.4	7.4	3.0	2.1	39.0	...	Free flame
2	0.4000 g. sod. arsenite + 1 g. sodium hydroxide......	10.8	7.6	3.2	24.8	41.1	...	Free flame
3	0.4000 g, sod. arsenite + 1 g. sodium hydroxide......	10.7	7.0	3.7	29.9	40.5	...	Free flame
4	0.4000 g. sod. arsenite + 1 g. sodium hydroxide......	11.5	4.4	7.1	11.5	43.8	30	325–340
5	1.0 g. sod. sulfite (38% sulfite) + 2 g. sodium hydroxide + 1 drop of water..............................	10.1	9.6	0.5	0.4	38.3	...	Free flame
6	1.0 g. sod. sulfite (38% sulfite) + 2 g. sodium hydroxide + 1 drop of water..............................	10.4	10.0	0.4	0.3	39.3	10	Free flame
7	0.2000 g. sod. nitrite + 1 g. sodium hydroxide + 1 drop of water..	9.3	9.3	0	0	35.5	25–30	320–355
8	1 g. ferrous sulfate (crystals) + 2 g. sodium hydroxide.	8.2	2.9	5.3	20.4	31.3	25	410
9	0.553 g. ferrous sulfate (crystals) + 2 g. sodium hydroxide...	10.7	7.0	3.7	17.1	40.6	15–20	410
10	0.7 g. cuprous chloride + 2 g. sodium hydroxide + 3 drops of water......................................	10	2	8	0	40	40–50	Free flame
11	1 g. nickel sulfate (crystals) + 2 g. sodium hydroxide..	10.8	10.8	0	0	41.0	25–30	400–450
12	1 g. manganous sulfate (crystals) + 2 g. sodium hydroxide...	10	3	7	0	40	30	400–450

13	1 g. cobalt sulfate (crystals) + 2 g. sodium hydroxide..	10	7	3	0	40	30	400–450
14	0.5 g. bismuth subnitrate + 1 g. sodium hydroxide....	8	8	0	0	32	10–20	Free flame
15	1 g. stannous chloride (crystals) + 2 g. sodium hydroxide.........	..	..	...	40	..	10	300–350
16	0.5 g. lead sulfate + 2 g. sodium hydroxide + 0.5 cc. of water.....	12	12	0	0	46	5	400–450
17	0.7 g. cupric chloride (crystals) + 2 g. sodium hydroxide.........	13	13	0	0	51	...	400–450
18	0.7 g. magnesium sulfate (crystals) + 2 g. sodium hydroxide.........	14.5	14.5	0	0	55	10	400–450
19	0.5 g. bismuth oxide + 2 g. sodium hydroxide + 2 cc. of water.........	13	13	0	0	50	...	300–350
20	Sodium antimonite + sodium hydroxide (amounts unknown).........	7.4	6.3	1.1	0.2	28.4	...	...
21	Titanous sulfate + sodium hydroxide (amounts unknown).........	9	9	0	1	34	...	...
22	Titanous sulfate + sodium hydroxide solution.....	3.6	3.6	0	0	13.7	...	Boiled
23	Cerous sulfate + sodium hydroxide..........	15	14	1	6	57	...	Free flame
24	0.5 g. mercurous chloride + 2 g. sodium hydroxide....	14	14	0	0	52.5	...	Free flame
25	0.5 g. vanadium sulfate + 2 g. sodium hydroxide.....	13.5	12	1.5	20	52	...	300–350
26	Uranous sulfate + sodium hydroxide solution........	8.5	8.5	0	0.8	32	...	Boiled

Description of Experiments.

The fusions were carried out in a hard glass tube (Pyrex glass was used in most of the experiments), of approximately 50 cc. capacity, bent in such a form as to catch the water which distilled off from the fusion mixture and prevent it from running back into the hot portion of the tube. This tube was provided with a rubber stopper carrying a small dropping funnel and a small bore tube leading to a water-jacketed gas buret containing mercury. This buret was provided with a two-way tap. Heating was effected by means of a bath of fused sodium nitrite which melts at 271° and can be used for temperatures up to 350°. For temperatures above 350° a bath of fused potassium dichromate was used. Below 350° the temperatures were recorded by an ordinary thermometer and above that temperature by a mercury thermometer under 60 atmospheres pressure of nitrogen in quartz.

The procedure consisted in placing a carefully weighed amount of substance in the bottom of the fusion tube, and adding quickly a known weight of sodium hydroxide in coarse powder, inserting the stopper and connecting with the gas buret. As gas was evolved in the reaction the levelling tube was lowered so that the pressure in the apparatus was always approximately atmospheric. After the fusion, water was run into the tube through the tap funnel and all the gas driven into the buret. The gas was then analyzed for hydrogen and oxygen and, where necessary, for other constituents, and in some cases the contents of the fusion tube was also analyzed in order to determine the amount of oxidation which had occurred. Oxygen was determined by absorption by phosphorus in a Hempel pipet and hydrogen by combustion with hot copper oxide contained in a small quartz tube heated to redness by a Bunsen burner the accuracy of this method for determining hydrogen having first been proved by the analysis of gas mixtures of known hydrogen content. For convenience and accuracy the gas buret was directly connected with the small quartz tube containing copper oxide, and this to the phosphorus pipet. The gas for analysis was first passed from the buret into the pipet, the quartz tube being at room temperature. This was repeated until all oxygen which remained in the quartz tube after the first passage had been absorbed. The copper oxide was then heated and the gas again passed over and back. The oxygen present in the apparatus at the start was calculated from the nitrogen remaining after the fusion.

The accuracy of the method for determining hydrogen was tested by preparing mixtures of hydrogen and nitrogen of known composition and analyzing them. The nitrogen was prepared from air by removing carbon dioxide and oxygen. The hydrogen was prepared electrolytically and freed from traces of oxygen by passing over hot copper.

	I. Cc.	II. Cc.
Nitrogen used	37.4	26.4
Hydrogen used	47.3	59.0
Hydrogen found	47.2	58.9

In order to determine whether any error exists in the application of this method to mixtures of hydrogen and oxygen, due to a union of hydrogen and oxygen induced by a union of phosphorus and oxygen, the following gas mixtures were analyzed:

	I. Cc.	II. Cc.
Air used	50.0	50.0
Oxygen in air	10.4	10.4
Hydrogen used	21.6	30.2
Oxygen found	10.4	10.4
Hydrogen found	..	30.2

Table I gives the details of the experiments.

The following table shows the results of the determinations of the extent of oxidation in the case of the above experiments with arsenious acid and ferrous sulfate. Col. I gives the volume of oxygen equivalent to the hydrogen evolved plus the free oxygen absorbed; Col. II the oxygen taken up by arsenite; Col. III that taken up by ferrous iron.

TABLE II.

Expt. No.	I. Cc.	II. Cc.	III. Cc.
1	4.1	6.6	..
2	15.6	19.0	..
3	18.7	21.2	..
9	12.3	..	12.5

The above values of the extent of oxidation of arsenite were determined by titration against standard iodine in the presence of sodium hydrogen carbonate. Oxidation of ferrous iron was determined by titration against standard permanganate in sulfuric acid solution. The values in Cols. I and II and I and III are substantially equal, showing that an equivalent oxidation has occurred.

Discussion.

In the experiments with sodium arsenite and ferrous sulfate the extent of the oxidation, as well as the amount of hydrogen evolved were determined. These were found to be equivalent.

In the case of stannous chloride, as well as of vanadium sulfate, much hydrogen was evolved, with cerous sulfate a less amount and with uranous sulfate only a small amount. The extent of the oxidation effected in these 4 cases was not measured.

It is interesting to observe that neither sodium nitrite nor sodium sulfite was oxidized. In view of the fact that sodium sulfite in water

solution is oxidized by free oxygen at ordinary temperature, and that both of these salts are rather easily oxidized in water solution by several oxidizing agents, this failure to undergo oxidation when fused with sodium hydroxide is noteworthy.

Upon examining the bases whose salts were oxidized it is observed that they belong, with the exception of iron, to Groups 4, 5 and 6 of the periodic table. Tin and cerium fall in Group 4; phosphorus, vanadium and arsenic fall in Group 5, while chromium and molybdenum fall in Group 6. If this has any bearing at all on the matter it is the more surprising that nitrogen and sulfur, which fall in Groups 5 and 6, respectively, are not oxidized from nitrites and sulfites to nitrates and sulfates. In this connection it would also be of interest, and especially in view of the industrial importance of the reaction in the manufacture of formates, to study the action of carbon monoxide with sodium hydroxide with a view to determine whether oxidation to carbon dioxide according to this general reaction occurs or not.

The mechanism of these reactions consists ultimately in the decomposition of water, the oxygen carrying the oxygen acceptor to a higher stage of oxidation and the hydrogen being evolved in the gaseous state. Reactions with fused or dissolved alkali hydroxides are described in the literature in which the other reacting compound acts as both oxygen and hydrogen acceptor, one mol being oxidized and one mol simultaneously reduced. In such cases the hydrogen, instead of being evolved in the free state, goes to reduce a second mol. These are in all probability special cases of the general oxidizing action of alkali hydroxides referred to in this paper, with probably the same mechanism involving the decomposition of water. The following are instances of this action: Ditte[1] observed that stannous hydroxide reacts with very strong solutions of potassium hydroxide at ordinary temperatures with the formation of tin and potassium stannate; also Rammelsberg[2] observed that lower phosphorus salts such as $NaH_2PO_2.H_2O$, when heated pass into phosphates and phosphine.

The evolution of hydrogen when many metals as aluminium, zinc, and lead are boiled with sodium hydroxide solution is no doubt initiated by this general oxidizing action of water catalyzed by sodium hydroxide.

$$Zn + 2H_2O = Zn(OH)_2 + H_2.$$
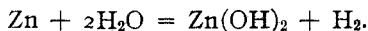
The inner mechanism of the catalysis of this general oxidizing reaction induced by alkali hydroxides, constitutes the working hypothesis which, as stated at the outset, led to this investigation. It has to do with the relationship between water and alkali hydroxide in the dissolved and

[1] *Ann. chim. phys.*, [5] **27**, 145 (1882).

[2] *Ber.*, **5**, 494 (1872).

fused states. A statement of this theory with experimental evidence and argument to support it will be presented in the near future.

Summary.

The general nature of the action of fused sodium hydroxide in effecting oxidations has been pointed out.

The reaction has been shown to involve ultimately a decomposition of water, one mol of oxygen going to effect oxidation and two mols of hydrogen being either evolved or fixed by a hydrogen acceptor.

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THE ACTION OF SODIUM HYDROXIDE ON CARBON MONOXIDE, SODIUM FORMATE AND SODIUM OXALATE.

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In a previous paper[1] we have shown that fused sodium hydroxide is very active in effecting oxidations. As pointed out there, it seemed desirable in the light of this fact to investigate more fully the action of sodium hydroxide upon carbon monoxide, sodium formate and sodium oxalate. The necessity for this became further apparent upon examining the literature with its confusing statements regarding the reactions involved.

It has long been known that carbon monoxide acts on sodium hydroxide to form sodium formate at moderately high temperatures. Merz Tibirica[2] recommended the use of moist carbon monoxide and loose soda lime at temperatures not above 220°. A commercial method described by Ullmann[3] consists in the use of producer gas at 6 to 8 atmospheres pressure acting on finely ground sodium hydroxide at 120–130°. Merz and Weith[4] have stated that a residue consisting of at least 70% oxalate and the remainder carbonate can be obtained by heating sodium formate rapidly to above 400° but that at about 360° the formation of carbonate is much greater. Levi and Piva[5] state that formate begins to decompose at 300°, that the decomposition is violent at 400° and complete at 550°. They give two analyses of the products which include small quantities of carbon dioxide, large amounts of carbon monoxide and hydrogen, carbonate and oxalate. The admixture of sodium carbonate is stated to bring about a quantitative yield of sodium oxalate

[1] THIS JOURNAL, 40, 1773 (1918).
[2] Ber., 13, 23 (1880).
[3] Ullmann, "Enzyklopädie der Technischen Chemie."
[4] Ber., 15, 1507 (1882).
[5] Ann. chim. applicata, 1, pp. 1–24.