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.

BY MAITLAND C. BOSWELL AND J. V. DICKSON.

Received August 15, 1918.

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

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[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.

from formate, without the necessity of particularly rapid heating or of heating above 360°. The investigators who took out the patent[1] based upon this observation, believed that it gave support to the following mechanism:

$$2HCOONa = Na_2CO_3 + H_2 + CO$$
$$CO + Na_2CO_3 = Na_2C_2O_4$$

However, the efficacy of the addition of carbonates in increasing the yield was called in question shortly afterwards,[2] it being stated that the yield claimed had not been reached in a great number of experiments that were tried. The addition of oxalate, however, was stated to be a marked improvement. Later[3] the addition of small amounts of sodium hydroxide (under 5%) to the formate was again claimed to have a good effect, technically pure oxalate being produced at a temperature below the melting point of the formate. With regard to the action of carbon monoxide on sodium hydroxide at high temperatures, Bain and Tyrrell[4] showed that no oxalate (or at most only traces) is formed at temperatures between 355° and 490°, carbon monoxide being used at atmospheric pressure. Dumas and Stas[5] found that sodium formate heated with barium hydroxide gives oxalate and hydrogen, and that oxalate heated with barium hydroxide gives carbonate and hydrogen. However, neither the temperatures nor the amounts of substances used were recorded.

The above statements show the unsatisfactory condition of the whole question from a scientific point of view, much of the work evidently having been done with a view solely to the commercial method of preparing oxalate.

The present investigation was undertaken with a view of ascertaining the action, if any, of carbon monoxide on sodium hydroxide at about the temperature of decomposition of sodium formate, with which it was thought the mechanism of the decomposition of the formate might be closely connected. In view of the oxidizing action of fused sodium hydroxide on various substances,[6] it was thought that the non-formation of oxalate from sodium hydroxide and carbon monoxide (at temperatures at which formate gives oxalate) might be due to the oxidation of the monoxide to dioxide (carbonate, of course, then being formed). Our experiments have shown this conjecture to be correct.

The oxidizing action of sodium hydroxide on carbon monoxide having been shown, it was thought desirable to determine the action of sodium

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[1] D. R. P. 111,078, *Z. angew. Chem.*, **1900**, p. 448.

[2] D. R. P. 144,150, *Ibid.*, **1903**, p. 924.

[3] D. R. P. 161,512, *Ibid.*, **1905**, p. 1793.

[4] E. J. Tyrrell, *Thesis*, Univ. of Toronto, 1917.

[5] *Ann. Chem.*, **35**, 129 (1840).

[6] This Journal, **40**, 1773 (1918).

hydroxide on formate and oxalate, particularly in view of the statement quoted above that small amounts of sodium hydroxide added to formate increase the yield of oxalate. The experiments described below show that at temperatures far below those at which formate or oxalate alone is decomposed with any degree of rapidity, fused sodium hydroxide carries them over rapidly to carbonate with the evolution of hydrogen.

In view of the oxidizing action of sodium hydroxide it was thought that the decomposition of pure sodium formate by heat might be initiated by dissociation of some of the formate into carbon monoxide and sodium hydroxide, which latter, reacting then with more formate and also, at higher temperature with the carbon monoxide would form oxalate, carbon dioxide and carbonate, all the sodium hydroxide being carried over to carbonate before oxidizing all the oxalate to carbonate. One experiment was performed in order to detect, if possible, such a dissociation, but the results were negative.

Experimental Work.

The apparatus used in all these experiments, with the exception of the last one, was similar to that used in previous fusions.[1] The carbon dioxide, oxygen and hydrogen were determined as already described. The carbon monoxide was determined by absorption by ammoniacal cuprous chloride solution. After removal of the hydrogen by hot copper oxide the gas was again passed into the potash pipet, the final residue being called nitrogen. This last treatment with potash would show the presence of any hydrocarbons or any carbon monoxide which might have escaped the cuprous chloride and which would have burned to carbon dioxide. The carbon dioxide found at this stage was never more than 0.2 cc. so that it did not affect the results appreciably.

Action of Sodium Hydroxide on Carbon Monoxide.

Two experiments were performed, the procedure being as follows: The sodium hydroxide was weighed out of a weighing bottle into a small glass tube about the size of a thimble which was quickly slipped down to the bottom of the fusion tube. The latter was stoppered quickly and connected with the gas buret. The end of the fusion tube was immersed in a bath of fused potassium dichromate which was kept at 410–430°. When the volume of air in the buret had come approximately to equilibrium, the delivery tube was closed with a pinchcock and disconnected from the buret. The air was expelled from the buret and a measured quantity of analyzed carbon monoxide was admitted in its place. The buret was again connected with the delivery tube, the pinchcock, however, closed. A water suction pump was attached to the tap funnel and the fusion tube evacuated. The carbon monoxide was then given access to the fusion tube. After heating for some time the tube was

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[1] This Journal, **40**, 1776 (1918).

allowed to cool and an excess of hot, boiled, dil. hydrochloric acid was drawn in through the tap funnel, and the gas driven over into the buret for analysis. The solution remaining in the tube was tested for oxalate. The results of these two experiments are as follows:

TABLE I.—ACTION OF SODIUM HYDROXIDE ON CARBON MONOXIDE.

NaOH used, g.	CO taken, cc.	CO used up, cc.	CO_2 produced, cc.	H_2 produced, cc.	O_2 used up, cc.	Time of heating.
1.000	47.0	25.8	26.5	23.1	0.5	30 min.
0.441	55.0	31.2	29.0	27.9	0.8	25 min.

No oxalate remained. The oxygen used up was found by subtracting the amount left after the fusion from the amount corresponding (in the composition of air) with the nitrogen present after the fusion, allowance being made for the nitrogen and oxygen content of the carbon monoxide. In determining the amount of carbon dioxide produced allowance had to be made for the carbonate in the alkali used, which was determined from time to time.

Decomposition of Sodium Formate by Heat.

The formate used was prepared by neutralizing sodium carbonate (Baker's C. P.) with excess of formic acid (Merck's), evaporating nearly to dryness on the water bath and drying at 110–130° in an oven. 0.2072 g. of formate was heated in a fusion tube connected with the gas buret at about 325° for 10 minutes. The decomposition being very slow the temperature was raised to about 345° where it was kept for 15 minutes. The tube was allowed to cool when it was seen that the volume of gas had increased only 3 cc. The tube was again heated for 30 minutes at 390–400° when the volume of gas increased considerably. The temperature was raised to 420° where it was kept for 10 minutes without much increase in the volume of gas. The gas, including the carbon dioxide from the carbonate, was displaced by the addition of dil. sulfuric acid and analyzed with the following results:

	Cc.
Hydrogen produced	17.0
Carbon monoxide produced	22.0
Carbon dioxide produced	21.7
Oxygen present at the start	10.4
Oxygen used up	4.4

The solution in the fusion tube was titrated with standard permanganate, giving a titer corresponding to 0.046 g. oxalate.

Action of Sodium Hydroxide on Sodium Formate.

This experiment was carried out in a manner similar to the previous one, 0.157 g. formate and 0.352 g. hydroxide being used. The temperature was 275°. The mixture began quickly to froth and within 5 minutes the reaction appeared to be complete. The heating was continued for 10 minutes. Analysis of the gas resulted as follows:

	Cc.
Hydrogen produced	47.9
Carbon dioxide produced	50.2
Carbon monoxide produced	0.3
Oxygen used up	0.1

No oxalate was found in the solution.

Action of Sodium Hydroxide on Sodium Oxalate.

The experiment was similar to the previous one, the temperature, however, being 290°. 0.1982 g. oxalate and 0.52 g. hydroxide were used. Here again the action appeared to be over in 5 minutes. The gas analysis gave the following results:

	Cc.
Hydrogen produced	27.9
Carbon dioxide produced	63.2
Carbon monoxide produced	0.1
Oxygen used up	0.0

The solution remaining required permanganate corresponding to 0.0025 g. oxalate.

Behavior of Formate at Lower Temperatures.

The following experiment was performed in order to detect, if possible, any dissociation of formate that might take place below the temperature of its ordinary decomposition.

About 0.2 g. of sodium formate was heated in a U-tube of hard glass about $^1/_4$ inch in diameter, having a small bulb at the bottom holding the formate. One end of the tube was closed by means of rubber tubing and a pinchcock, and the other end attached to the gas buret. The bulb was heated in an oil bath to 150° and then gradually during more than an hour to about 315° where it was kept for 20 minutes. While still hot, air was drawn through the tube and the gas drawn into the buret. The gas in the buret was analyzed with the following results:

	Cc.
Oxygen used up	0.1
Hydrogen produced	0.8
Carbon monoxide produced	0.7
Carbon dioxide produced	0.2

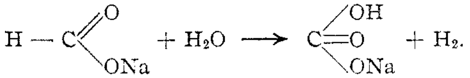
Discussion of Results.

The main reaction of sodium hydroxide upon carbon monoxide is evidently the oxidation of carbon monoxide to carbon dioxide with the liberation of a corresponding amount of hydrogen.

$$CO + H_2O = CO_2 + H_2.$$

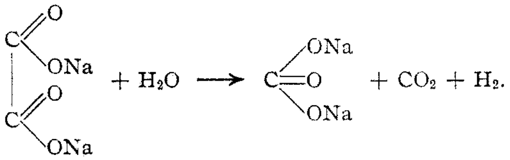
If this were the sole reaction, the volumes of carbon monoxide used up, dioxide produced, and hydrogen produced would be equal. The oxygen used up may be considered as having carried twice its volume of monoxide to dioxide so that the 3 volumes, carbon monoxide, carbon dioxide and hydrogen concerned in the main reaction in Expt. 1 when corrected for this will be, respectively, 24.8 25.5 and 23.1 cc.; and in Expt. 2, 29.6, 27.4 and 27.9 cc. While these volumes are not quite equal in either case they are near enough to indicate that the main reaction is an oxidation with the liberation of an equivalent amount of hydrogen.

The fusions of sodium hydroxide with formate and oxalate show that the latter are carried rapidly and almost completely to carbonate at temperatures far below their ordinary decomposition temperatures,



$$H-C\begin{matrix}\nearrow O\\ \searrow ONa\end{matrix} + H_2O \longrightarrow C\begin{matrix}\nearrow OH\\ =O\\ \searrow ONa\end{matrix} + H_2.$$

With excess of sodium hydroxide this sodium hydrogen carbonate is carried to carbonate.



$$\begin{matrix}C\begin{matrix}\nearrow O\\ \searrow ONa\end{matrix}\\ |\\ C\begin{matrix}\nearrow O\\ \searrow ONa\end{matrix}\end{matrix} + H_2O \longrightarrow C\begin{matrix}\nearrow ONa\\ =O\\ \searrow ONa\end{matrix} + CO_2 + H_2.$$

With excess of sodium hydroxide the carbon dioxide is fixed as carbonate. Tyrrell[1] and Bain found that sodium oxalate decomposed very slowly at 465° and lower. According to these equations the oxidation of formate to carbonate is accompanied by the formation of carbon dioxide and hydrogen in equal volumes. In the experiment the hydrogen is found to be 2.3 cc. less than the carbon dioxide. The latter (50.2 cc.) accounts for 0.1525 g. formate although 0.1570 g. was used. In the oxidation of oxalate to carbonate the hydrogen formed is by the equation $^1/_2$ of the carbon dioxide and we find in the experiment it is 3.7 cc. short of this. Carbon dioxide formed (63.2 cc.) accounts for 0.1890 g. oxalate, while the amount remaining undecomposed according to the permanganate titration is 0.0025 g., 0.1915 g. out of 0.1982 g. thus being accounted for.

The practice of mixing sodium hydroxide with sodium formate to the extent of 5% in the manufacture of oxalate from formate according to D. R. P. 165,512 can now be given an interpretation. Pure sodium formate, when heated alone, undergoes decomposition at a very slow rate at temperatures below about 400°. At this temperature the chief reaction is the formation of carbonate and carbon monoxide with very little oxalate. At temperatures up to 480° there is considerable carbonate formed with a corresponding poor yield of oxalate. If, however, a small amount of sodium hydroxide is present the temperature of fusion is low, and at this temperature the oxidation from formate to oxalate occurs with the evolution of an equivalent amount of hydrogen, the temperature

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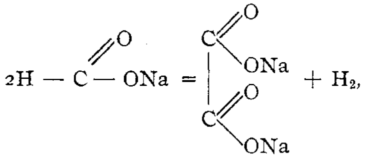
[1] Bain and Tyrrell, *Loc. cit.*

however, being so low as to keep the velocity of the oxidation of formate and oxalate to carbonate small. That is, the transformation from formate to oxalate in the presence of a small amount of sodium hydroxide as carried out in practice in the manufacture of oxalate is really an oxidation of formate by the water present in the fusion, the hydrogen being evolved in the free state. That is the direct source of the hydrogen evolved is not the sodium formate as represented in the usual reaction equation

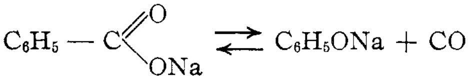


$$2H-\overset{\displaystyle O}{\overset{\|}{C}}-ONa = \begin{array}{l} C(=O)ONa \\ | \\ C(=O)ONa \end{array} + H_2,$$

but the water present. This may be considered as an oxidation of an acid, whose anhydride is carbon monoxide to an acid whose anhydride is the hypothetical oxide C_2O_3, with the evolution of an equivalent amount of hydrogen.

$$2CO + H_2O = C_2O_3 + H_2.$$

This immediately raises the question of the mechanism of the fusion of carboxylic acid salts in general with sodium hydroxide. It seems highly probable that these actions as far as they involve the replacement of carboxyl by hydrogen (and apart altogether from those secondary reactions recognized as oxidations such as the formation of *p*-oxybenzoic acid in the case of the fusion of sodium benzoate and sodium hydroxide), are all oxidations catalyzed by sodium hydroxide and involving the elements of water. In the production of methane and benzene from sodium acetate and sodium benzoate the oxidation product, sodium carbonate, is formed. The hydrogen, however, instead of being evolved as such is fixed by the methyl and phenyl groups, respectively, and appears, not as free hydrogen, but as methane and benzene. However, some of the hydrogen escapes this action and appears as free hydrogen, for it is a well-known fact that the methane prepared by this process may contain as high as 8% of free hydrogen. The mechanism in the case of the fusion of sodium benzoate and sodium hydroxide (as far as it concerns the production of benzene) would accordingly be



$$C_6H_5-C\begin{array}{l} {}^{\nearrow O} \\ {}_{\searrow ONa} \end{array} \rightleftarrows C_6H_5ONa + CO$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$C_6H_5ONa + H_2O + H_2 \longrightarrow C_6H_6 + NaOH + H_2O.$$

It seems that in general the primary and chief action of sodium hydroxide in fusion actions is an oxidizing one with the mechanism referred to. Whether this action is accompanied by the evolution of free hydrogen or not depends on whether any compound is present which can act as hydrogen acceptor and thus prevent, completely or in part, its evolution in the free state.

Summary.

When carbon monoxide is heated with excess of sodium hydroxide at temperatures at which formate is transformed into oxalate, oxidation almost quantitatively to carbon dioxide occurs with the evolution of approximately an equivalent amount of hydrogen.

At temperatures far below those at which formate and oxalate alone are decomposed, sodium hydroxide carries both of them almost quantitatively to carbonate with the evolution of equivalent amount of hydrogen.

The general reaction involving the replacement of the carboxyl group by hydrogen in alkali fusions probably involves simultaneous oxidation and reduction by the oxygen and hydrogen of water.

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THE FUSION OF SODIUM HYDROXIDE WITH SEVERAL PHENOLS AND SULFONIC ACIDS.

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In view of the widespread application of sodium hydroxide fusions in organic chemistry both in the laboratory and in the factory, we decided to investigate some of them in the light of the oxidizing action already treated of in two previous papers[1,2] dealing with this subject. The present paper gives the results of our investigation of this reaction in the case of sodium benzene sulfonate, β-naphthalene sulfonate, anthraquinone β-monosulfonate, sodium salt of phenylglycine-*o*-carboxylic acid and of the 7 phenols, carbolic acid, hydroquinone, pyrocatechine, resorcin, pyrogallol, oxyhydroquinone and phloroglucine.

Considerable work done in this laboratory had already shown that the fusion of sodium benzene sulfonate with sodium hydroxide under widely varying conditions failed to give a yield of phenol in excess of 90% of the theory. The discovery of the widespread applicability of sodium hydroxide in effecting oxidations, made it appear that in this property of sodium hydroxide might be found the secret of the failure to obtain a greater yield. This involved the study of the gas changes occurring in the fusion with sodium hydroxide of sodium benzene sulfonate and of sodium phenate, in the presence and absence of free oxygen. It soon

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[1] THIS JOURNAL, 40, 1773 (1918).

[2] *Ibid.*, 40, 1779 (1918).