drogen 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).

became evident that the evolution of hydrogen in both of these reactions is conditional upon this reaction being preceded by an oxidation by free oxygen. In the case of several separate fusions of sodium hydroxide with these two compounds, the ratio of hydrogen evolved to free oxygen absorbed was approximately one-half. The inference is that free oxygen carried the sodium phenate over to some polyhydroxy phenol, which was then oxidized in the sodium hydroxide fusion according to the general reaction under discussion, with the evolution of free hydrogen. This naturally led to a study of the fusion reaction of the 6 dihydroxy and trihydroxy benzenes with sodium hydroxide. It also led to an investigation of the effect upon the yield of phenol, of conducting the fusion of sodium benzene sulfonate out of contact with free oxygen, with the result that it was found possible to increase the yield of carbolic acid in this way by about 8% and thus make the yield approximately theoretical.

In view of this marked increase in yield it seems that manufacturers of phenol should consider the feasibility of conducting the fusion out of contact with atmospheric oxygen.

Although the yields of β-naphthol in the presence and absence of free oxygen were not compared, yet the fact that oxidation (as indicated by evolution of hydrogen) occurs only when free oxygen is present, makes it appear highly probable that an increased yield would be obtained by carrying out the reaction in the absence of free oxygen.

Experimental.

The fusions were performed in the same manner and with the same apparatus as already described in a previous paper,[1] with the additional precaution that the residual gas after combustion with hot copper oxide, and measurement, was passed into a potassium hydroxide pipet to determine whether any carbonaceous gas had been present in the original gas. In almost all cases the carbon dioxide found was quite small and thus the error introduced may in consequence be neglected.

In Expts. 7 and 8 oxygen was admitted to the fusion tube only after the main reaction was over (quiet fusion) 10 and 18 minutes, respectively, from the outset.

In order to determine the effect of excluding free oxygen upon the yield of phenol in the fusion of sodium benzene sulfonate and sodium hydroxide, two experiments were conducted, one in an open crucible with access to the air, and the other in a closed crucible in an atmosphere of nitrogen.

The sulfonate used was made by the usual lime method and recrystallized. The actual sulfonate content was determined by extraction of a weighed amount under a reflux condenser with boiling 95% alcohol, filtering, evaporating in a dish, and weighing.

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[1] This Journal, 40, 1773 (1918).

TABLE I.—GAS ANALYTICAL RESULTS.

No.	Wt. of substance. G.	Wt. of sodium hydroxide. G.	Temperature. Degrees	Oxygen			Hydrogen produced. Cc.	"Methane" produced. Cc.	Time of heating. Mins.	Ratio oxygen used to hydrogen produced.	Nitrogen present. Cc.
				at the start. Cc.	at the end. Cc.	used up. Cc.					
Sodium Benzene Sulfonate.											
1	1	1	300–330	9.8	2.6	7.1	3.1	0.5	40	2.3	37.2
2	1	2.5	300	9.9	3.4	6.5	3.2	0.5	35	2.0	37.6
3	1	2.5	290	9.4	4.6	4.8	2.6	0.2	40	1.9	35.5
4	1	2.5	350	9.5	2.5	7.0	3.9	0.3	40	1.8	36.1
5	1	2.5	325	35.3	10.9	24.4	12.6	0.4	30	1.9	37.5
6	1	2.5	325	75.7	7.1	68.6	37.4	0.7	60	1.8	16.2
7	1	2.5	325	42.0	12.0	30.0	16.7	0.6	40	1.8	40.8
8	1	2.5	325	20.4	1.5	18.9	9.5	0.9	75	2.0	77.3
9	1	2.5	325	1.0	0.5	0.5	0.6	0.0	30	...	37.6
10	1	2.5	325–355	1.0	0.5	0.5	0.3	0.2	..	...	39.6
Sodium Phenolate.											
11	1	2	330	10.0	1.9	8.1	5.7	0.2	40	1.4	37.9
12	0.64	2.5	335	11.2	2.1	9.1	6.1	0.4	45	1.5	42.3
13	1	2	315–340	10.6	0.3	10.3	6.1	0.2	40	1.7	40.1
14	1	2	315–335	1.0	0.4	0.6	0.6	0.3	..	...	34.3
Sodium Sulfite.											
15	1	2	Flame	10.4	10.0	0.4	0.3	..	10	...	39.3
16	1	2	300	10.1	9.6	0.5	0.4	..	..	...	38.3
Sodium Naphthalene Sulfonate.											
17	1.28	4.5	300	9.6	2.8	6.8	2.9	0.1	40	2.3	36.4
18	1.28	4.5	275–315	0	0	0	0.4	0.1	30	...	45.4
Sodium Anthraquinone Monosulfonate.											
19	1	4.5	275–295	12.4	1.9	10.5	6.5	0.1	35	1.6	47.1
20	1	4.5	280–310	1.0	0.5	0.5	15.2	1.0	30	...	52.7
Sodium Phenylglycine-*o*-carboxylate.											
21	0.65	*	230–270	11.3	3.6	7.7	13.8	0.2	30	0.6	42.7
22	0.65	*	265	0.5	0.1	0.4	2.5	0.1	35	...	58.0
Pyrocatechine.											
23	0.5	2.0	315	10.2	4.0	6.2	4.5	0.4	30	1.4	38.8
24	0.5	2.0	340	2.5	1.2	1.3	1.7	0.7	..	...	39.4
Resorcin.											
25	1	2	315–330	10.3	3.5	6.8	4.2	0.5	..	1.6	39.1
26	0.5	2	350	1.5	0.6	0.9	0.4	0.1	40	...	41.4
Hydroquinone.											
27	0.5	2	325	10.9	1.9	9.0	6.7	1.0	60	1.3	41.3
28	0.5	2	340	1.0	0.2	0.8	0.5	0.1	40	...	35.7
Oxyhydroquinone.											
29	0.5	2	350	10.3	1.3	9.0	25.2	8.7	55	0.4	40.6
30	0.5	2	...	0	0	0	16.0	3.6	60	...	53.0
Pyrogallol.											
31	0.5	2	350	11.0	1.5	9.5	6.6	1.7	55	1.4	41.6
32	0.5	2	330	0	0	0	1.7	0.2	55	...	64.1
Phloroglucin.											
33	0.5	2	340	9.8	6.5	3.3	6.0	24.0	45	0.5	37
34	0.5	2	280–340	1.0	0.4	0.6	2.0	27	50	...	67

* 1.5 g. NaOH + 1.5 g. KOH.

The method of fusion and isolation of the phenol was as follows: 70 g. of sodium hydroxide was heated in a small iron crucible to above 400° for 15 minutes. It was then allowed to cool to 330°. 100 g. of dry sodium benzene sulfonate of known sulfonate content was added with constant stirring, during a period of 30 minutes, the temperature being kept at 330° for 10 minutes after the addition of all the salt. The fusion mixture was poured on an iron plate, powdered in a mortar and dissolved in 250 cc. of water. This solution was treated with sulfuric acid, (1 : 1 by weight), until distinctly acid. Care was taken to stir the phenol layer well into the acid as previous experiments had shown that considerable loss may arise due to the solution of phenolate in the separated phenol layer. The phenol was separated by means of a separating funnel and distilled. The first runnings were caught in a small separating funnel, the phenol layer separated and returned to the distilling flask. The fraction boiling between 175–185° was caught in a small weighed beaker.

Extraction with ether of the water layer after separation of phenol gave 5 to 7 g. of phenol in several determinations. In the calculations below, 6 g. is added to the phenol actually obtained in each case, thus giving a close approximation to the actual yield of phenol produced in the fusion.

The following are the results obtained by fusion in air:

Wt. of phenol	36.3 g.	35.9 g.
Phenol dissolved in the water layer	6.0	6.0
	42.3	41.9
Sulfonate content	89%	89%
Theoretical yield of phenol	46.48 g.	46.48 g.
Actual yield	91.1%	90.1%
Average yield		90.6%

The fusion in an atmosphere of nitrogen was conducted according to the same procedure with the exception that oxygen was excluded. This was accomplished by covering the iron crucible with an asbestos cover which was provided with a hole sufficiently large to add the salt and to stir. A stream of nitrogen was led in through a glass tube projecting through the cover, during the fusion process and while the product was cooling. The following are the results obtained:

Weight of phenol	40.0 g.
Phenol dissolved in water layer	6.0
	46.0
Theoretical yield	46.5
Actual yield	99.0%

Discussion.

In the benzene sulfonate fusion Expts. 1 to 8 inclusive in which free oxygen was present, oxygen was used up and hydrogen produced in approximately the proportion 1 : 2, notwithstanding that very varying amounts of oxygen disappeared in the several experiments. In these experiments very small amounts of methane were formed. In Expts. 9 and 10, where no free oxygen was present, practically no hydrogen or methane was produced. Apparently under the conditions of the experiments sodium hydroxide is almost without action on phenol in the absence of free oxygen.

Expts. 11 to 14 inclusive with sodium phenolate are parallel in their results with those of the fusion of the sulfonate, that is, hydrogen is formed only when free oxygen is used up, and practically no methane is produced. That is, under the conditions of the experiment sodium hydroxide is almost without action on sodium phenolate in the absence of free oxygen. This fact together with the results of Expts. 7 and 8, where oxygen was admitted to the sulfonate fusion only after the main reaction had occurred, makes it appear very probable that the oxidation of phenolate is the chief, if not the entire cause, of the secondary reaction in the case of the sulfonate fusion.

Expts. 15 and 16 show that sodium sulfite (also a product in the sulfonate fusion) is practically unacted on by sodium hydroxide in the presence of air under the conditions of the experiment.

It follows that in the fusion of the sulfonate in the presence of air the first action is the taking up of free oxygen by the phenolate formed, to produce some compound (or compounds) which is then oxidized by the water present in the fusion with the evolution of hydrogen according to the general reaction under discussion.

The fact that the ratio of oxygen used up to hydrogen produced is in all cases so nearly constant and approximately equal to 2 in the sulfonate fusions, indicates that the compound sought may have been formed from phenol by the introduction of two oxygens, which compound is then oxidized by the "water reaction" with the evolution of one volume of hydrogen. The experiments with the 6 dihydroxy and trihydroxy phenols were performed in order to determine, if possible, whether any of these react with sodium hydroxide in such a way as to point to one or more of them taking part in the mechanism of this reaction. An inspection of results of Expts. 24, 26, 28, 30, 32 and 34 shows that in the absence of free oxygen, with the exception of oxyhydroquinone, practically no hydrogen is evolved. This eliminates 5 of the phenols as possible intermediate products. In the case of oxhydroquinone (Expt. 30) although much hydrogen is evolved, there is also considerable methane, which eliminates this compound as a possibility. Hence none of the dihydroxy or trihydroxy phenols are involved in this mechanism.

It is of interest to observe that the oxidation of the 3 dihydroxy benzenes as well as pyrogallol by fused sodium hydroxide occurs only when free oxygen is present. The reaction involving the elements of water is not involved in these fusions under the conditions employed.

In the case of sodium β-naphthalene monosulfonate the results recorded in Expts. 17 and 18 are quite similar to those of sodium benzene sulfonate; that is, hydrogen is evolved only when free oxygen has been taken up.

In the case of sodium anthraquinone sulfonate recorded in Expts. 19 and 20 the results are different from the preceding cases in that the hydrogen produced does not depend on the previous absorption of free oxygen.

In the case of the sodium salt of phenylglycine *o*-carboxylic acid the absorption of oxygen is necessary before an evolution of hydrogen occurs.

In a recent paper[1] on the oxidation of ethyl alcohol by soda lime Carroll has shown that the oxidation is due in the main to the sodium hydroxide in the soda lime, and that fused sodium hydroxide is more active in oxidizing alcohol than soda lime. In discussing the mechanism of the conversion of ethyl alcohol to sodium acetate Carroll expresses the belief that the reaction consists in splitting off the hydrogen from the ethyl alcohol and acetaldehyde, the sodium hydroxide acting as catalyzer for these dissociations. In the oxidation of acetaldehyde to acetic acid Carroll assumes the intermediate formation of keten and the subsequent addition reaction of the keten and sodium hydroxide to form sodium acetate. In view of the fact there is no evidence of the formation of keten in this reaction, and of the fact that alkali hydroxide can act simultaneously as both oxidizing and reducing agent (as for instance with the compounds benzaldehyde, *o*-chlorophenol, phenol at high temperatures, stannous hydroxide, etc.) it seems simpler and more in harmony with the facts to represent the reaction as involving the elements of water, the oxygen being used to oxidize the compound, and the hydrogen being fixed or evolved in the free state, depending on whether a hydrogen acceptor is present or not.

In a recent paper[2] Witzemann has studied the action of potassium permanganate in effecting the oxidation of acetone in the presence of alkali hydroxide, and finds that the extent of the oxidation is largely dependent on the concentration of the latter. Witzemann moreover observes that the permanganate used is somewhat less than corresponds to the oxidation produced, and in discussing the mechanism of reaction

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[1] *J. Phys. Chem.*, **22**, 128 (1918).

[2] THIS JOURNAL, **39**, 2657 (1917).

comes to the conclusion that one possible explanation is the reduction of the manganese dioxide (presumably by the organic compounds present) to manganous oxide which latter is then reoxidized by the oxygen of the air, and superposed on this an oxidation of the acetone, catalyzed by the alkali. Witzemann however says nothing regarding the nature of this latter action. The fact that numerous oxidations occur (which form the subject of this series of papers) in which sodium hydroxide acts as catalyzer to a general reaction involving the elements of water, the hydrogen being either evolved in the free state or fixed by some hydrogen acceptor, may afford an explanation of this observation of Witzemann. From this point of view acetone or one or more products of its oxidation may be further oxidized by this reaction involving the decomposition of water, either the maganese dioxide or permanganate acting as hydrogen acceptor. The fact, as Witzemann points out, that sodium hydroxide alone or permanganate alone is without action, but in conjunction effect the oxidation, makes it appear at least a possibility that a large part of the total oxidation reaction is due to this reaction of water, the permanganate and (after the reaction has set in), the manganese dioxide, acting as hydrogen acceptors.

Further support for this view regarding the mechanism of oxidations in general in alkaline solution will be presented by one of us in the near future.

Summary.

It has been determined that the yield of carbolic acid by the fusion of sodium benzene sulfonate with sodium hydroxide is increased by about 8% and made approximately theoretical by carrying out the entire fusion and cooling of the melt in an atmosphere free from gaseous oxygen.

When the fusion is performed in the absence of free oxygen no hydrogen is evolved and practically the only action occurring is that represented by the equation

$$C_6H_5SO_3Na + NaOH = C_6H_5ONa + NaHSO_3.$$

In the presence of free oxygen secondary reactions occur involving first an absorption of free oxygen followed by an oxidation involving the elements of water, free hydrogen being evolved.

A study of the oxidations of the 6 di- and tri-hydroxy benzenes by sodium hydroxide showed that none of these could be the direct cause of this hydrogen evolution.

The oxidation of the 3 di-hydroxy benzenes and of pyrogallol by sodium hydroxide occurred only in the presence of free oxygen. Oxidation by reaction with water catalyzed by sodium hydroxide was not observed.

This last observation is also true in the case of the fusion of sodium β-naphthalene sulfonate as well as of phenylglycine *o*-carboxylic acid with sodium hydroxide.

In the fusion of sodium anthraquinone β-monosulfonate with sodium hydroxide, oxidation occurs by means of the water reaction without the necessity of a previous oxidation by free oxygen.

It seems highly probable that the yield of β-naphthol would be increased by carrying out the fusion of the corresponding sulfonate with sodium hydroxide in the absence of free oxygen.

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THE ADSORPTION OF ARSENIOUS ACID BY FERRIC HYDROXIDE.

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In the course of the investigation of the catalysis of certain reactions by silicic acid and ferric hydroxide gels, the large adsorption of arenious acid from solutions of sodium arsenite by ferric hydroxide was encountered.

Bunsen and Berthold[1] observed the great adsorption power of ferric hydroxide for arsenious acid, and considered the combination to be a basic ferric arsenite. Biltz[2] studied the reaction quantitatively and concluded that it was a case of adsorption and not chemical combination, since it followed the "adsorption law" expressed by the empirical and very flexible equation $E = \beta A^p$, where E is the concentration of adsorbed substance in the absorbing phase, A is the concentration of absorbed substance in solution at equilibrium, and β and p are constants. Lockmann and Paucke[3], and Lockmann and Lucius[4] studied the conditions under which the adsorption of arsenious acid from solution is complete. A comparison made in the latter paper shows that a given amount of arsenious acid is removed from solution by a considerably smaller amount of precipitate, when an exactly stoichiometric amount of ammonia is used than when twice that amount is used. They also observed that the adsorption of arsenious acid is considerably reduced by the use of potassium hydroxide or sodium hydroxide instead of ammonia. Mecklenburg[5] worked with ferric hydroxide and arsenious acid in demonstrating his principle of "affine Adsorptionskurven," *i. e.*, adsorption curves so related, each by a particular factor, to a unit curve, that the ordinate corresponding to any given abscissa on one of the curves may be obtained by multiplying, by the factor, the ordinate on the unit curve correspond-

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[1] "Das Eisenhydroxyd," 1834.

[2] *Ber.*, **37**, 3138 (1904).

[3] *Z. Chem. Ind. Kolloide*, **8**, 273 (1911).

[4] *Z. Physik. Chem.*, **83**, 735 (1913).

[5] *Ibid.*, **83**, 609 (1913).