tion-products are obtained which are similar but not identical with the product obtained in the reaction with nitrobenzene alone. These substances appear to take part in the reaction. No aminophenolsulfonic acid is obtained.

The black products reduce in each case to form vat dyes from which cotton is dyed. The product from nitrobenzene dyes cotton a steel-gray. That from the aminoanthraquinone gives a brown vat oxidizing on cotton to a heliotrope. The anthraquinone product dyes cotton steel-gray. The product obtained with anthracene is less readily reduced than the others mentioned and dyes cotton brown. None of these dyes are fast to boiling alkalies.

The average yield of *p*-aminophenol-*o*-sulfonic obtained was about 10% of the theory.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

A HYDRATE OF ANTHRAQUINONE 2,7-SODIUM SULFONATE.

BY M. L. CROSSLEY.

Received October 20, 1916.

In a previous communication,[1] the author has shown that in the separation of the sodium salt of the mono-β-sulfonic acid of anthraquinone and the salts of the 2,6- and 2,7-disulfonic acids, in mild acid solution, a salmon-pink substance of very striking properties is obtained. It is a very sensitive indicator and is unlike any anthraquinone sulfonate thus far described. Its chemical activity is very marked. It forms unstable products with ethyl alcohol, chloroform, and toluene.

The natural assumption, in view of the dissimilarity of the substance to other anthraquinone compounds, was that it was formed from some impurity in the anthraquinone. The evidence against this view, at the very outset, was strong. In the first place, the yield was 9 g. from 50 g. of anthraquinone. In the second place, the product was not obtained by other methods of separating the acids. Chemically pure anthraquinone from two sources was crystallized several times from glacial acetic acid and then from benzene, but it still gave the salmon-pink compound. Analysis of the compound showed that it contained at least 14 carbon, 2 sulfur, and 2 sodium atoms.

Calc. for $C_{14}H_8O_9S_2Na_2$: C, 39.07%; H, 1.86%; O, 33.50%; S, 14.88%; Na, 10.69%. Found: C, 39.17; H, 1.93; O, 33.32; S, 14.85; Na, 10.73.

The substance gives the anthranol test. When fused with potassium hydroxide it gives 1,2,7-trihydroxyanthraquinone. It is clear from this evidence that the anthraquinone nucleus is present in the substance. It is also certain that there are two sulfonic groups in the 2,7-positions

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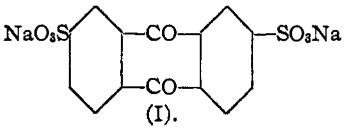
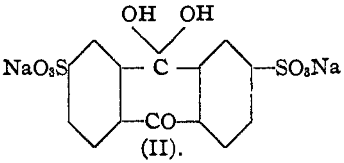
[1] THIS JOURNAL, 37, 2178 (1915).

and that the substance is a disodium salt. The compound, however, is not identical with anthraquinone 2,7-sodium sulfonate. The evidence supports the formula $C_{14}H_6O_8S_2Na_2.H_2O$. The water is not held, however, as water of crystallization which can be driven off by heating the compound but it is in union as a hydrate.

The chemical behavior of the compound suggests that it is an addition product formed by the union of one molecule of water and one molecule of the sulfonate, the addition having taken place through either the sulfonic or carbonyl oxygen. It seems probable that the addition concerns a carbonyl grouping. The substance itself is salmon-pink while the 2,7-sulfonate is ruby-red. A change of the bonding of the carbonyl carbon from double to single would be expected to diminish the color. Addition at this point would best account for the properties of the substance.



(I).



(II).

The stability of the compound, on heating it, is a serious objection to the above formula. It is true, however, that our knowledge of the influence of neighboring groups on a carbon to which is attached two hydroxyls is limited. If the hydrate is to be represented by Formula II, the sensitiveness of its neutral solutions to mild alkalies might be explained by the assumption that one of the hydrogen atoms of the two hydroxyls is replaced by metal. The fact that sunlight reverses this change tends to support the assumption.

When the substance is suspended in ethyl alcohol and exposed to sunlight it changes to a dark green compound. This is unstable and changes back to the pink substance when removed from the alcohol.

Addition appears to be a much more common factor in chemical reactions than is always evidenced by the ultimate products obtained. There are many cases in which it is the initial and important step in the molecular changes that take place in the formation of new compounds. In this connection, the theory of chemical reaction and reactivity as advanced by Baly[1] is worthy of careful and thorough consideration. It should be of considerable service in the future progress of chemistry.

Summary.

The pink compound isolated in the separation of 2,6- and 2,7-sulfonic acids of anthraquinone analyses for $C_{14}H_8O_9S_2Na_2$.

Its properties prove it to be a hydrate of anthraquinone 2,7-sodium sulfonate, the addition taking place, probably, through one of the carbonyl oxygens.

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[1] THIS JOURNAL, 37, 979 (1915).

Addition in one of the carbonyl groups would best account for all the properties of the substance.

While it is to be expected that water would split off from a compound containing a carbon atom united with two hydroxyls, our knowledge of the behavior of such a group in the neighborhood of other radicals is limited and a hydrate of the 2,7-sulfonate such as indicated is not impossible.

Addition appears to be represented in many chemical reactions.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE IDENTIFICATION OF ACIDS.

BY E. EMMET REID.

Received September 21, 1916.

Progress in the investigation of natural products and in the analysis of artificial mixtures depends greatly on the possibility of preparing crystalline derivatives of the substances under investigation. We have satisfactory crystalline derivatives of aldehydes and of alcohols in the phenylurethanes and α- and β-naphthylurethanes, and of aldehydes in the phenylhydrazones and substituted phenylhydrazones.

As organic acids occur in natural products in great variety and have been produced synthetically in immense numbers, their positive identification is of the utmost importance. Usually the amides, anilides and *p*-toluides are relied upon for the identification of acids, but, in some cases, these are difficult to prepare.

It is desirable to have several series of derivatives so that if one fails in a particular case, another may be available. In important cases, in order to avoid the possibility of error, it is often necessary to prepare several different derivatives. Hence, a new series of crystalline derivatives, which are readily made from acids, may be of use.

p-Nitrobenzyl bromide was prepared by Wachendorf[1] in 1877 by heating *p*-nitrotoluene and bromine in a sealed tube. He found that it reacted readily with sodium acetate to give the acetate m. p. 78°.

Now a derivative of acetic acid, which is formed readily from sodium acetate, crystallizes well, is not too soluble in alcohol, and melts sharply at a conveniently high temperature, is very desirable as a means of isolating and identifying acetic acid. It seems remarkable that advantage has not been taken of this observation. The identification of organic substances was not so much an object in Wachendorf's time, and his work seems to have been overlooked. His statements about the ready formation of *p*-nitrobenzyl acetate suggested the present work. It was thought that other *p*-nitrobenzyl esters might likewise be formed readily and might have convenient properties.

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[1] *Ann.*, **185**, 266 (1877).