sulphur. Chilling boiling sulphur in ether gives 44.1 per cent. of the insoluble form.

(10) It is shown by identity in boiling-points under ordinary and reduced pressures and identity in specific gravities that sulphur which will give the insoluble form when chilled is identical in constitution near the boiling-point with that which will not.

(11) It is shown by identity in solubility between 120° and 160° that the two kinds of sulphur mentioned in (10) are identical in constitution also below the transition point of $S\mu$ to $S\lambda$ (160)°.

(12) The facts referred to in (10) and (11), together with the conclusions of the preceding paper showing the identity of the two kinds of sulphur at the transition point (160°) itself, demonstrate that the insoluble form is present in all specimens of melted sulphur in proportions depending upon the temperature alone, whether by treatment with ammonia or otherwise they have lost the capacity to give insoluble sulphur by chilling or not.

(13) The conclusion is reached that amorphous sulphur is supercooled $S\mu$—the form stable above 160°.

(14) With pure sulphur, freed from sulphur dioxide by recrystallization or by treatment with carbon dioxide above 310°, or by treatment with ammonia or hydrogen sulphide at any temperature at which it is fluid, the $S\mu$ reverts so rapidly to the soluble form that it cannot be supercooled. When traces of sulphur dioxide, iodine and other substances are present, $S\mu$ is more or less completely supercooled and gives amorphous sulphur. The way in which the latter class of foreign substances produces this effect is still being investigated.

(15) The close analogy of these phenomena to those observed in the cooling of cast iron and steel is pointed out.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF ORGANIC SUBSTANCES CONTAINING OXYGEN WITH NITRIC, SULPHURIC AND CHLORSULPHONIC ACIDS.

BY D. McINTOSH.

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THE basic properties of organic compounds containing oxygen have been discussed in a number of articles,[1] and the quadrivalence

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[1] *J. Chem. Soc.* (London), **85**, 919 (1904); **85**, 1098 (1904).

of the oxygen atom has been advanced as an explanation of the constitutions of the compounds formed. In all cases previously investigated the compounds had low melting-points, above which temperatures decomposition took place, with the formation of substituted products. Cohen and Gatecliff[1] have lately described additive compounds of the ethers with nitric acid, obtained, however, only as liquids, which were prepared at relatively high temperature. The existence, at such temperatures, of compounds in which the oxygen functioned as a tetrad, seemed so unlikely that I have made some experiments on the additive compounds of nitric acid with ether, alcohol, and acetone, and at the same time have endeavored to obtain compounds with a di-basic acid (sulphuric) and with chlorsulphonic acid.

The organic substances were purified by the usual method; to prepare the nitric acid, a mixture of nitric and sulphuric acids was distilled under reduced pressure, as described by Velley and Manley;[2] it contained probably 99.8 per cent. of acid.

Experiments with nitric acid.—The compounds were prepared by slowly adding the acid at —50° to the organic liquid cooled to —80°. The amount of heat evolved was small compared with that given out during the formation of similar compounds with the hydrogen halide, but larger than if addition compounds[3] with the halogen were formed. A white compound soon makes its appearance on the addition of acid to ethyl ether. It melts at —25°, and at a little higher temperature oxidation begins. At room temperature the action is violent, so that the bodies investigated by Cohen and Gatecliff must have contained water; and the agreement with the formulae given, in the case of the ethyl ether at least, must have been accidental.

A great many analyses of the ether-nitric acid compound were made, but with unsatisfactory results. For each molecule of ether the analyses showed between one and two molecules of acid present. It is possible that the compound is $C_4H_{10}O,2HNO_3$ and that it is contaminated by various products formed by oxidation of the ether.

More definite results were obtained with ethyl alcohol and with acetone. The former gave a white crystalline compound melting at —30°. This product contained 53.8, 53.9, 53.9 per cent. HNO_3,

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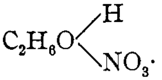
[1] *Chem. News*, **90**, 265 (1904).

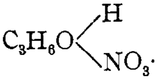
[2] *Trans. Royal Soc.*, **A191**, 363 (1898).

[3] *J. Chem. Soc.* (London), **87**, 784 (1905).

while in C_2H_6O,HNO_3, 57.8 per cent. acid is present. Since the compound was washed several times with alcohol, the low value for the nitric acid can be readily explained. The probable constitution is  $C_2H_6O\langle^{H}_{NO_3}$.

A similar compound, melting at —18°, was made from acetone. The analyses were:

Preparation I: 56.7, 51.0, 50.9 per cent. nitric acid.
" II: 54.1, 53.8, 53.0 per cent. nitric acid.

As $C_3H_6OHNO_3$ requires 54.1 per cent. of acid, the constitution is doubtless  $C_3H_6O\langle^{H}_{NO_3}$.

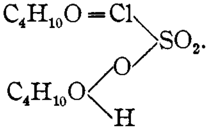
Experiments with Sulphuric Acid.—Anhydrous sulphuric acid made from the ordinary and the fuming acid dissolves readily in the cooled organic liquids with evolution of heat. No crystalline compounds were produced, but only syrupy liquids. This is strange, since phosphoric and sulphuric acids[1] give compounds with the much weaker basic substances, phenol and benzoic acid.

Experiments with Chlorsulphonic Acid.—This acid was prepared from sulphuric acid and phosphorus pentachloride and was redistilled; it did not freeze at —80°.

Alcohol instantly decomposed the chlorsulphonic acid, ethyl sulphuric and hydrochloric acids being formed. With ether and acetone white crystalline compounds were obtained, the former melting at —45°, and the latter at —30°. The analytical results were calculated from the total acid found, although the chlorine was also determined. The percentages of acid, in the case of the ether compound, were:

Preparation I: 43.9, 44.3;
" II: 45.8, 46.0;
" III: 42.4, 42.8;

while $C_4H_{10}O$, $HClSO_3$ contains 47.1 and $(C_4H_{10}O)_3$, $HClSO_3$ 34.4 per cent. The probable constitution[1] is:



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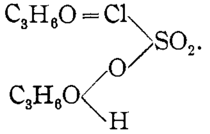
[1] Hoogewerff and Van Dorp: *Rec. trav. chim.*, **21**, 349 (1902),

The analyses of the acetone compound gave:

Preparation I: 47.3, 47.0;
" II: 48.4, 49.0.

A compound consisting of two molecules of acetone and one of acid has 50.1 per cent. acid, so that the product is $(C_3H_6O)_2,HClSO_3$, and its constitution is:



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May, 1905.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

ON CHLORONIUM SALTS.

BY JULIUS STIEGLITZ AND EDITH E. BARNARD.

Received June 12, 1905.

BAEYER'S epoch-making investigations[1] on the question of the constitution and the source of color of the triphenylmethane dyes, which grew out of his great work on oxonium salts, have been followed with especial interest by the one of us, because the results promised to throw light on three fundamental questions, in which he has been interested. In 1899[2] attention was called to the necessity of a careful investigation of the question whether the salts of certain carbimide derivatives, such as the imido-esters, are ammonium salts, $R_2C : (\underset{+}{N}RHX)$, or true salts (not esters or ester salts) of carbon ions $R_2\overset{+}{C}(NH_2)$. All the experimental evidence favoring the latter view, the existence of carbon ions, $R_3\overset{+}{C}$, was suggested and adopted, their formation was supposed to be greatly favored by the presence of imide groups but not limited to imide derivatives[3]. The question, however, is an exceedingly delicate one and physico-chemical measurements carried out since with imido-esters[4] have again raised doubts as to the correctness of the conclusion reached, and we are now inclined rather to the view that the salts are really ammonium salts and

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[1] *Ber.*, **35**, 1189, 3013 (1902); **36**, 2774 (1903); **37**, 597, 2818, 3191 (1904); **38**, 569 (1905).

[2] *Am. Chem. J.*, **21**, 101 (1899).

[3] *Loc. cit.*, p. 111.

[4] The results will be published shortly.