

large amounts of *perfectly colorless crystals*, which have remained unchanged for several months.

## THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF THE HALOGEN ACIDS WITH BENZENE DERIVATIVES CONTAINING OXYGEN

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In a paper on the basic properties of oxygen<sup>1</sup> von Baeyer and Villiger say: "While the substitution of positive groups, such as the alkyls, for the hydrogen in water makes the oxygen basic this is not the case with negative groups like phenyl. Phenyl, benzophenone, etc., do not give salts with acids. This is in full agreement with the behavior of ammonia derivatives, etc."

This generalization is not justifiable, for we shall show in this paper that benzophenone and other oxygen substances containing the phenyl group form complexes almost as readily as do ether, ketone,<sup>2</sup> etc.

Archibald<sup>3</sup> has made an extended study of the electrical conductance of organic compounds dissolved in the halogen hydrides, and in our effort to produce additive compounds we have been largely guided by his results; for it appears almost certain that conduction of organic substances in liquefied hydrobromic or hydrochloric acid is brought about by their union with the acid and the subsequent ionization of the compound. High conducting power in general means the formation of a large amount of the compound, and under proper conditions these addition products may be separated and analyzed.

*Experiments with Hydrogen Bromide.*—Nitrobenzene, phenol, anisol, phthalic acid, hydroquinone, and pyrogallol are only slightly soluble in liquefied hydrobromic acid, and under the conditions of experiment give no compounds. Benzoin, the cresols, thymol, salicylic acid, naphthol and benzyl alcohol are soluble and probably form compounds in solution, which, however, could not be separated. Resorcinol, benzophenone and benzoic acid give compounds which crystallize readily. They are all colorless substances with sharp melting points well above that of hydrobromic acid ( $-86^{\circ}$ ) and they form supersaturated solutions.

*Resorcinol compound*, melts  $-71^{\circ}$ ; analyses—sample I, 77.8 and 76.8 per cent. acid; sample II, 75.6 and 77.4 per cent. acid.  $C_6H_4(OH)_2 \cdot 4HBr$  contains 74.6 per cent. acid.

*Benzoic acid compound*, melts  $-44^{\circ}$ , 56.7, 59.0, 56.4 per cent. acid was found.  $C_7H_5O_2 \cdot HBr$  contains 57.2 per cent.

<sup>1</sup> *Ber.*, **33**, 1438 (1900).

<sup>2</sup> Walker, McIntosh and Archibald, *J. Chem. Soc.*, **85**, 1098 (1904). Vorländer, *Ann.*, **341**, 1 (1905).

<sup>3</sup> *THIS JOURNAL*, **29**, 665, 1416 (1907).

*Benzophenone compound*, melts  $-42^{\circ}$ , showed 73.5, 72.7, 75.0 71.5 per cent. acid.  $(C_6H_5)_2CO_6HBr$  has 72.8 per cent.

*Experiments with Hydrogen Chloride.* Nitrobenzene, benzoin, anisole, phenol, phenetol, benzoic, phthalic and gallic acids are insoluble or sparingly soluble in liquefied hydrochloric acid. Thymol, salicylic acid, naphthol ( $\alpha$  and  $\beta$ ) benzyl alcohol, benzaldehyde and cresol are soluble and probably form compounds, but these were not obtained as solids. Resorcinol and benzophenone gave compounds melting below  $-85^{\circ}$ . The resorcinol complex contained about 52 per cent. acid, which corresponds to three or four molecules of hydrogen chloride to one of resorcinol. The benzophenone hydrochloride contained 56.8 per cent. acid while  $(C_6H_5)_2CO \cdot 7HCl$  has 58.4 per cent. The benzophenone compounds differ from the corresponding ones of the fatty series which contain a much smaller proportion of acid. There are, however, indications of simpler addition products.

*Ethyl Ether and Hydrobromic Acid* unite to form a compound containing one molecule of each substance and here the oxygen has been assumed to be tetravalent. Since on electrolysis in a hydrobromic acid solution the ether moves to the cathode, the ether hydrobromide has been given the

constitution  $C_4H_{10}O \begin{matrix} \nearrow H \\ \searrow Br \end{matrix}$ , its molecular weight, however, being unknown.

A second compound,  $C_4H_{10}O \cdot 2HBr$ , probably exists (previous paper) in which, as in some acid salts of dimethyl pyrone, the oxygen may be taken as hexavalent. In the compounds of benzophenone and the halogen acids the latter are present in greater amounts than would be expected were the oxygen tetra- or even hexavalent. While the constitutions of such complexes might possibly be systematized by the assumption of the union of the acid with the carbon<sup>1</sup> it seems better, at present, to class them merely as substances with acid of crystallization.

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## TWO-COMPONENT SYSTEMS.

### PAPER I. ETHER-HYDROBROMIC ACID, ETHER-CHLORINE AND ETHER-BROMINE.

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While studying the compounds formed by organic substances containing oxygen with the halogens and with the halogen hydrides, I found it necessary to map out completely or in part several of these two-component systems. The results of three are given in the following pages.

The freezing-point determinations were made in a modified Beckmann apparatus with a platinum stirrer and a pentane thermometer, graduated

<sup>1</sup> Gomberg, *Ann.*, 370, 142 (1909).