

OXONIUM COMPOUNDS.—By D. McINTOSH, M. A., D. Sc.,
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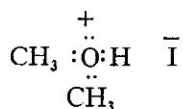
(Read by title 14 May, 1924)

Two contributions to theoretical chemistry have stimulated greatly the interest taken in molecular ² compounds. First, the views of Werner, expressed at length in his "Neuere Anschauungen auf den Gebiete der anorganischen Chemie," and the electron theory of valence (Thomson, Lewis and Langmuir). Amongst the compounds formed by the union of two well defined molecules, the oxonium group has undergone numerous investigations. Friedel, Collie and Tickle, and Baeyer and Williger have contributed to our knowledge of these complexes, and have shown that the ordinary view of the valency of oxygen as two must be modified, and that this number must be increased on occasions to four or even to six. This conception of quadri-valent oxygen, common to chemistry for the last twenty years, has been amplified by the electron theory of valency, so that many compounds whose constitutions were previously obscure, can now be represented graphically with, at least, some small degree of probability.

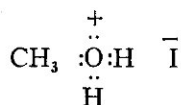
It appears that a little light is thrown on the mechanism of solution, catalysis, substitution and ionization by a study of these intermediate compounds. We stressed twenty years ago the view that in many instances ionization is preceded by chemical combination², a view which now has many adherents. Combination in solution is often indicated by the failure of Raoult's law, and is not infrequently a partial explanation for an apparent anomaly. For instance, water is insoluble in ether and in hydrobromic acid at low temperature, but is easily soluble in a mixture of the two, and from this solution a compound³ of the three components can be isolated. Acetic acid forms no compound with alcohol, and the production of an ester takes place very slowly. But a compound is formed from alcohol, acetic and hydrobromic

1. See Pfeiffer. *Organische Moleklüverbindungen*. The only serious omission noticed in this book is that of the excellent and comprehensive work of G. Baume.

acid, the molecules are probably brought nearer together, and the chemical reaction takes place more rapidly. Acetic acid forms no compound with acetaldehyde and polymerization does not take place. Hydrochloric acid forms a compound, probably quite complex, and paraldehyde is rapidly produced. Hydriodic acid forms the complex



with ether, and alcohol and methyl iodide are produced on standing. Then the alcohol unites with the acid forming



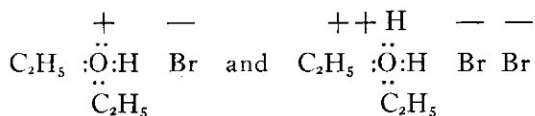
and methyl iodide and water are the final product. The importance of these intermediate compounds has been recognized from the time Van't Hoff published his "Ansichten ueber organische Chemie," and has been emphasized by no one more forcefully than by Armstrong in his numerous articles. My interest in these oxonium compounds is largely with two simple classes, one containing the halogen hydrides, and the other the halogens, in combination with organic substances containing oxygen. I shall describe a few of these compounds isolated recently, and shall suggest possible formulae for typical members of both these groups.

These two classes differ in many respects. The halogen compounds show only a very small heat of formation, while the others evolve from fourteen to twenty thousand calories for each gram molecule. The halogen hydride complexes conduct the electric current in solution and are therefore dissociated; the halogen compounds are not ionized. The molecular conductivity increases with concentration⁴, and this has formed

2. Walker, McIntosh and Archibald, Jour. Chem. Soc. 85, 1098 (1904).
3. Maass and Russel. Trans. Roy. Soc. (Canada) 13,259 (1919).

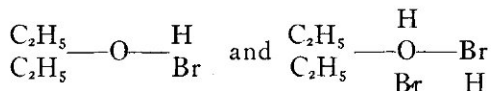
the starting point for a theory of complexes in solution. Finally, on electrolysis the organic molecule moves to the cathode, thus showing direct combination between it and the hydrogen of the acid.

On the electron theory of valence these compounds, can for the most part, be easily represented. For instance: C_4H_{10} , O. HBr and C_4H_{10} , O. 2 HBr can be written:

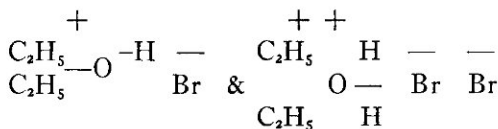


The hydrogen atoms share the electrons with the oxygen and give to the group a single or a double charge; the electrons from the hydrogen complete the bromine octets, which are, consequently, negatively charged. The bromine ion and the positively charged groups are held together by the electrostatic force. These two compounds were isolated many years ago.

It is well, I think, to emphasize the similarity between earlier formulae postulating quadrivalent or sexivalent oxygen and newer views. These compounds were previously written:



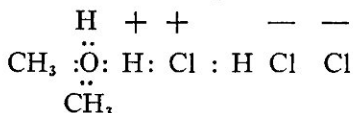
and in solution:



In an analogous manner the graphical formulae of the alcohol, ketone, and ester complexes may be written without any extension of the octet theory. Even the electrons in the rather involved compounds ($CH_3 COO C_2H_5$), 5 H Br can be satisfactorily grouped. The compounds⁴ mentioned by Lowry as

4. Steele, McIntosh and Archibald, Phil. Trans. (A) 205,99, (1905).
5. Jour. Chem. Soc. Industry, 43.218. (1924).

“disturbing” must differ from those just described since liquefied hydrogen chloride has a low Eotvos constant⁶, and is presumably, associated. If Lewis’ views on the sharing of two electron pairs by hydrogen be accepted this difficulty disappears.

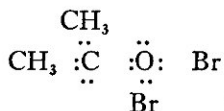


COMPOUNDS WITH THE HALOGENS

Comparatively few of these compounds have been made, but our investigations⁷ have shown no exceptions to the following rules for saturated⁸, aliphatic molecules:

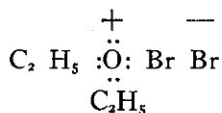
1. A mono-acid alcohol unites with one halogen atom.
2. A ketone or an ether unites with two⁹.
3. An ethereal salt (an acetate) unites with three halogen atoms.

The ketone complex can have the constitution



and calls for no further comment.

The oxides present more difficulty. Lewis suggests the formula



since Plotnikof has shown that a solution of ether in bromine conducts the electric current.

6. Steele, McIntosh and Archibald, loc. cit.

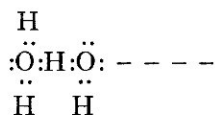
7. McIntosh, Jour. Chem. Soc., 85.919. (1905).

8. I except Schutzenburger’s compound, $\text{C}_4\text{H}_{10}\text{O} \text{ Br}_3$ which always contains a large amount of acid.

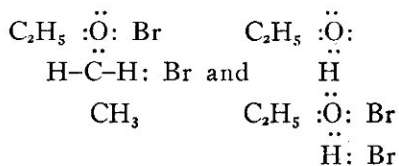
9. With ethylene oxide. See Maass and Boomer, Jour. Am. Chem. Soc. 44.1709 (1922).

We have shown¹⁰ that an ether-bromine mixture even when made at a comparatively low temperature and with the greatest care always contains hydrobromic acid, and we ascribed the conduction to the acid. Plotnikof replied to this with perhaps more heat than the question merited. However, the analogous compound with chlorine shows no conduction¹¹, and for this reason I look on Lewis' formula as incorrect.

Substances such as hydrogen flouride, the alcohols, water, acetic acid, etc., which show association in the liquid or gaseous state have, according to Lewis, a di-valent hydrogen atom. Water can be represented as:



If we accept this view—and of its convenience there can be no doubt—we may write for the ether-bromine and the alcohol-bromine compounds the formula:



and perhaps a better view of the substitution of bromine in ether is indicated in this representation than in any other.

Further the unstable compounds containing a halogen or hydrobromic acid and toluene may be easily represented if we admit the possibility of a halogen atom being shared, but the pairing of the inactive hydrogen atom of a methyl group seems too great an assumption to make. It must be remembered that these very unstable addition compounds are formed only in the neighborhood of -90°C . Possibly the determination of the molecular surface energy at low temperature might decide this point. Such a formula has the merit

10. Johnson and McIntosh, *Jour. Am. Chem. Soc.*, 31,1138 (1909).

11. Mennie and McIntosh, *Trans. Roy. Soc. (Canada)*, 16,303. (1922).

that it indicates the easy substitution of chlorine or bromine; benzene gives no compounds with hydrobromic acid.¹²

EXPERIMENTAL

A few typical compounds have been made and analysed with the object of testing somewhat further the rules given for the combination of the halogens and organic substances. These complexes do not differ from those previously made. They melt at low temperatures, are formed with a slight heat evolution, and when substitution is prevented do not conduct. The methods employed have been given in previous papers.

Normal propyl alcohol. This hydroxide gives compounds with both the halogens. With bromine the solution is so viscid that it is impossible to trace the freezing point curve or to obtain the compound pure enough for even an approximate analysis. Chlorine gives a white, crystalline compound, melting below -80°C . The analysis show 35.3, 38.1 per cent. chlorine; propyl alcohol with one atom of chlorine contains 37.2 per cent. No compound could be made with iso-propyl alcohol.

Normal and isobutyl alcohols. No compounds were obtained, due perhaps, to the syrupy solutions. The halogens appear to act more quickly on the iso-alcohols at low temperatures than on the normals.

Methyl ethyl ketone. The chlorine compound contained 43.6, 45.9 per cent. halogen. Required for two halogen atoms, 49.7 per cent. The bromine complex melted at -32° . Found 65.4, 64.4 bromine. For two bromine atoms 69.0 per cent. is necessary.

Methyl acetate. The chlorine compound melts at -70° . It contained 58.0, 57.4 per cent. chlorine. $\text{CH}_3\text{COOCH}_3\text{3Cl}$

Note.—I have said nothing of a new view—the group molecule. This conception seems to be of doubtful value as far as the oxonium compounds are concerned, but convenient and useful in a discussion of the combinations of the hydrocarbons.

12. Maass and Russel, loc. cit.

has 59.0 per cent. *Methyl acetate-bromine*. This substance was found to contain 77.3, 78.7 per cent. bromine; one with three bromine atoms requires 76.4 per cent.

Normal propyl acetate. The compound melted at -38° , and contained 67.7, 66.4 per cent. halogen. The tribrom acetate requires 70.2 per cent.

The chlorine addition product was made, but its melting point was so low that it was not analysed.

Isoamyl acetate. The chlorine compound contained 45.2, 43.1 per cent. For three atoms of chlorine 45.0 is required. The corresponding bromine substance could not be made.

It will be noticed that the difficulty in making the oxonium compound increases with the complexity of the organic component. Perhaps the mobility of the hydrogen atom is largely responsible for the existence of compounds such as $\text{HBr} \cdot 4\text{H}_2\text{O}$, etc.

Substitution takes place quickly in acetoacetic ether even at a very low temperature. Knorr¹³ has shown that in this ester the enol and keto forms are in equilibrium. Possibly compounds could be made from the keto isomeride.

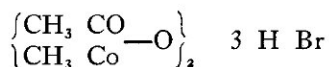
Acetic anhydride. The 94 per cent. material was separated from acetic acid by cooling to a low temperature, and then fractionated repeatedly, the part distilling between 139° and 140° being retained. This had a density of 1.0753 at $20^{\circ}/4^{\circ}$ and froze at -72° . Walten and Withrow¹⁴ give a freezing-point of -86° to this anhydride.

Apparently compounds were formed with both halogens. They were analysed, and the complete freezing point curves determined. But neither method fixed their exact compositions; for the maxima on the curves showed compounds containing three halogen atoms, while the analyses indicated only two. This point will be examined later.

13. B. B. 44,1138 (1911).

14. Jour. Am. Chem. Soc. 45,2690. (1923).

While some doubt exists of compound formation with the halogens, acetic anhydride readily unites with hydrobromic acid. Considerable heat is evolved when the anhydride is added to the liquefied acid, and the mixture is an excellent conductor of electricity. A white crystalline compound, (M.P.—5°) separates out, and shows on analysis 52.1 per cent. acid. It is probably:



which contains 54.3 per cent. This rather complex combination¹⁵ is of the same type as certain compounds of the halogen hydrides with acetic acid.

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MAY, 1924.

15. Jour. Am. Chem. Soc. 45, 28,538. (1906).