The results here reported were obtained with mutually calibrated flasks, burets and pipets and are believed to be accurate to ±0.02 cc.

Summary

The determination of bromates in the presence of ferric iron was studied, three methods proposed and their applicability demonstrated experimentally.

1. Iodimetric Method. Phosphoric acid solutions containing sodium pyrophosphate in which the dissociation of the resulting iron complex to give ferric ions is less than in the presence of either reagent alone, were analyzed for their content of bromate by the addition of potassium iodide in excess and titration of the liberated iodine with sodium thiosulfate. The time rate of reduction of bromate by potassium iodide with various concentrations of phosphoric acid was determined. The necessary variation in the concentration of phosphoric acid and sodium pyrophosphate with increasing amounts of ferric iron was determined.

2. Oxalate-Permanganate Method. The bromate was reduced by excess sodium oxalate in boiling sulfuric acid solution in the presence of mercuric perchlorate and the excess oxalate determined by titration with potassium permanganate. It was shown that this reaction furnishes the basis of an improved method for iodimetric standardization using sodium oxalate as primary standard.

3. Ferrous Sulfate-Permanganate Method. This involved the same procedures as in the Oxalate-Permanganate Method except that ferrous sulfate was substituted for sodium oxalate and titration was effected cold instead of in a hot solution.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY]

OXONIUM COMPOUNDS IN THE VAPOR STATE. METHYL ETHER—HYDROGEN CHLORIDE

BY O. MAASS AND D. M. MORRISON

Received May 2, 1923

Organic compounds containing oxygen have been shown to form complexes with the halogen hydrides; these are known as oxonium compounds. For reasons which are discussed below, further work dealing with their stability is of interest. In the investigation which is the subject of this paper, methyl ether and hydrogen chloride were mixed in the gaseous state with the object of determining whether or not association of these molecules occurred.

A thorough investigation of oxonium compounds has been made by D. McIntosh[1] and some of his co-workers. In one of his papers[2] on the sub-

---

[1] McIntosh, THIS JOURNAL, **27**, 26, 1013 (1905); **33**, 71 (1911).

[2] *Ibid.*, **34**, 1273 (1912).

ject, properties of these compounds were reviewed with the object of comparing the oxonium complexes with the so-called molecular compounds such as water or alcohol of crystallization. The conclusion arrived at was that these oxonium compounds were very stable. They are simple, that is, generally 1 molecule of organic liquid unites with 1 molecule of acid. The melting points of the compounds are far above the melting points of the constituents; also, the behavior on electrolysis and the magnitude of the heats of formation serve to distinguish the oxonium compound from the ordinary solvent of crystallization.

The existence of these compounds is definitely established in the solid state; as they melt, dissociation into the original molecules takes place. Conductivity experiments[3] indicated that this was not at all complete, but the validity of this derived interpretation is not absolutely certain. If it could be definitely shown that a measurable amount of association exists in the liquid or gaseous state, the character of the oxonium compound would at once be established as comparable to that of ammonium chloride.

This is of particular interest since in the past the structure of the oxonium compound has been given by assigning a valence of 4 and in some cases[4] 6 to the oxygen atom; this is not in agreement with the present theory of the structure of the atom and consequent ideas of valence.

Methyl ether and hydrogen chloride form an oxonium compound melting at —96°; the liquid boils lower than —12°. It is, therefore, possible to mix these two as gases above this temperature. The methyl ether and hydrogen chloride were prepared and purified as previously described[5] and the boiling points were shown to be in exact agreement with those previously found.

The experimental procedure consisted in mixing a definite volume of hydrogen chloride with an equal volume of methyl ether in a container having exactly twice this volume. The pressures of the unmixed hydrogen chloride and methyl ether were the same; hence, after the gases were mixed any decrease in pressure would indicate association or increase in molecular attraction; which of these two would be the cause of the change, if any took place, would then be established in the manner described further on.

The accompanying diagram (Fig. 1) will serve to illustrate the manner in which the required amounts of methyl ether and hydrogen chloride were mixed.

The hydrogen chloride was condensed in the bulb M; the pressure tap L made it possible to keep it liquid at the temperature of a mixture of solid carbon dioxide and ether. The construction of this tap is shown in the diagram. The stopper, of large

---

[3] THIS JOURNAL, **35**, 535 (1913).

[4] Ref. 2, p. 1279.

[5] THIS JOURNAL, **44**, 1709 (1922).

diameter, is surrounded at the bottom by a space which may be evacuated and then closed off by means of the tap O, thus being held in place by the pressure of the atmosphere. The area exposed to atmospheric pressure in this way is large as compared to that exposed to the vapor pressure of the hydrogen chloride and taking into account the angle at which this latter pressure is applied, some 30 atmospheres' pressure in the bulb may be withstood, yet the stopper turns easily. The tap L is connected through a pentoxide tube and the 2-way tap H to the main apparatus. The volumes up to the tap H could be swept out as indicated in the diagram.

The methyl ether was condensed in Bulb N which is similarly connected to the main apparatus, except that on account of its high boiling point, no pressure tap was necessary.

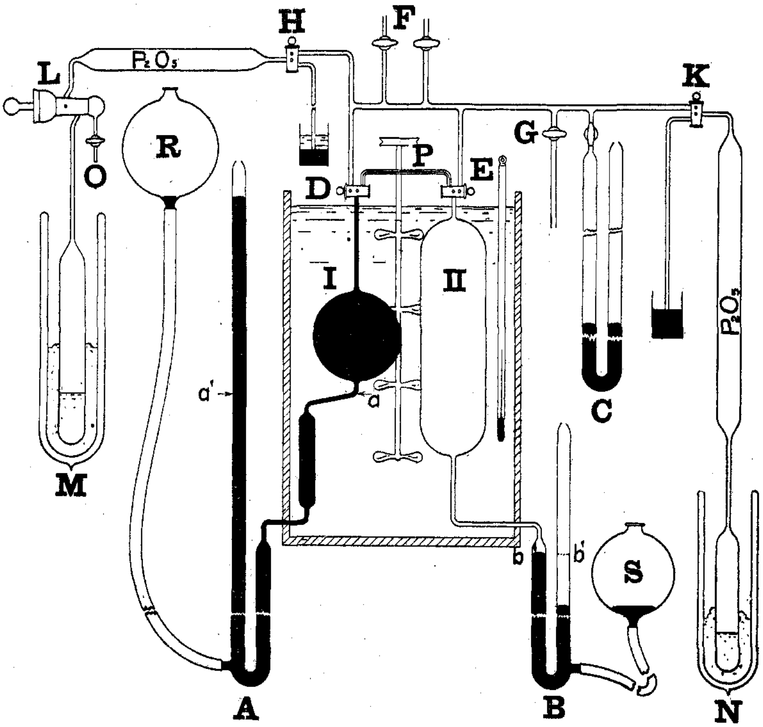

Fig. 1

Two reservoirs, I and II, were contained in a bath, the temperature of which could be kept constant. Each reservoir was connected to a manometer (A and B, respectively) in which the mercury could be raised or lowered. These reservoirs were connected through 2-way taps, D and E, to the glass-tube system which could be evacuated through Taps F and filled with air through Tap G. The volumes of I and II were chosen such that II measured from Point b was exactly twice that of I measured from Point a. This was tested by completely evacuating I and II, filling I with air at atmospheric pressure, and sending this into II, through the capillary tube P by raising Reservoir R until the mercury filled I up to Tap D. This was repeated, while the temperature was kept constant, and it was found that the mercury in both arms of manometer B was level when it reached the height b. Obviously with this procedure no corrections need be applied to the gas laws.

The actual experiments were then carried out as follows. Reservoirs I and II and all connected tubing were thoroughly evacuated. Reservoir I was filled with hydrogen chloride until the pressure registered by manometer C was slightly above atmospheric. The reservoir R was then raised until the mercury reached level a, while Tap G was gradually opened to the atmosphere. This insured that the volume of hydrogen chloride in I, when the mercury was at the level of aa′, was exactly at atmospheric pressure, which was read on a barometer. Taps D and E were then turned in such a way that the hydrogen chloride was completely transferred to II by raising Reservoir R. E was then closed, the tubing and Reservoir I again evacuated and the process repeated with methyl ether.

If no changes occurred on mixing when the mercury was brought up to Level b by means of Reservoir S, the level of the mercury in the other arm would be the same, namely, b′. Association would mean a diminution in pressure in Reservoir II, the magnitude of which could be measured to 0.1 mm. by Manometer B. Care was of course taken to keep the temperature constant throughout an experiment, and the barometer was read to make sure that no changes in atmospheric pressure had occurred. The latter was usually found to be the case as only about an hour was required to complete an experiment.

For reasons which will be stated later, it was desirable to carry out experiments in which the original pressure of the unmixed hydrogen chloride and methyl ether was lower than atmospheric and in other cases where these two pressures differed from one another. This was done by reading these pressures by means of Manometer C, care being taken always to bring the level of the mercury in Reservoir I up to Level a, when the pressure in C was read.

The bath was kept constant at any desired temperature between 30° and —10°. The portion of Reservoir II which is part of the manometer and outside of the bath was less than 0.1% of the total volume, so that any small difference in temperature in this small volume could not have an appreciable effect on the measurement.

The first experiment showed than when the two gases were mixed a considerable lowering of pressure took place, which increased with lowering of temperature. The full lowering was not reached immediately upon mixing the gases, and it was thought that this might be due to the fact that a reaction with measurable velocity occurred. When methyl ether was put in first and followed by the hydrogen chloride, about half an hour was required for the establishment of equilibrium; on the other hand, when the hydrogen chloride was put in first this time was reduced to half, the final pressure being exactly the same in either case. This showed that the greater part of this equilibrium time was due to the time required for complete diffusion to take place because when the heavier methyl ether was put in last uniform mixing took place more rapidly, as the gases entered Reservoir II at the top. Dry hydrogen chloride does not act on pure mercury and once equilibrium was established no further change in pressure occurred.

On the assumption that the contraction results from the formation of an oxonium compound which exists in equilibrium with hydrogen chloride and methyl ether according to the equation, $HCl + (CH_3)_2O = (CH_3)_2OHCl$, it is possible to calculate the amount of association in the following way.

Let v = the volume of Reservoir I; Then $2v$ is that of Reservoir II. Let v contain n gram molecules, P be the pressure of the unmixed gases and p the final pressure of the mixture.

The number of gram molecules in the mixture equals then, $n\ (2-x)^x$, where X = amount associated; now, $n = \frac{Pv}{RT}$.

$$n\ (2-x)^x = \frac{2pv}{RT}$$

Therefore, $X = 2\left(1 - \frac{p}{P}\right)$ (1)

Table I contains the results of experiments at various temperatures, the initial pressure in every case being atmospheric.

Table I

Values of X and k Calculated from Experimental Data

Temp. °C.	Pres. of unmixed gas P	Pres. of mixt. p	X Calc.	k Calc.
−10.15	762	543.2	0.5742 ?	..
− 7.65	756	613.1	.3780 ?	..
− 5.3	756	663.2	.2454 ?	..
0	760	689.5	.1854	2720
4.2	758	691.8	.1746	2958
9.2	758	702.2	.1472	3745
18.8	756	713.53	.1124	5299
29.2	763	730.7	.0846	7557

In Fig. 2 the variation of the dissociation with the temperature is shown graphically. It is apparent that the assumption upon which the calculation of the dissociation is based is certainly not justified at the lower temperatures. The graph shows plainly that in the neighborhood of —4° something approaching a discontinuity occurs. At that temperature the condensation point for the mixture, 1 hydrogen chloride:1 methyl ether,

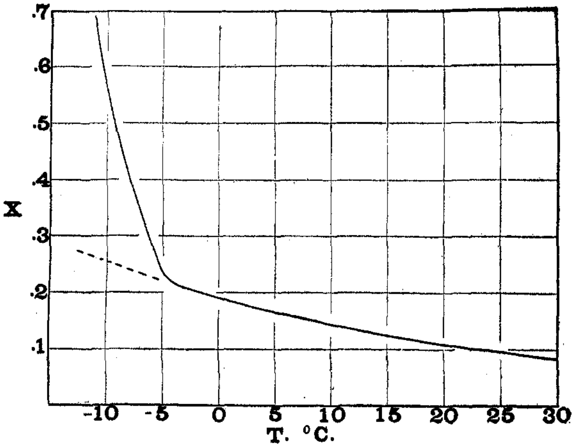

Fig. 2

is approached and the aberrations from the gas laws of this mixture will mask any effect due to association of the molecules.

It might be argued that all the diminutions in pressure when the gases are mixed might be due to a similar cause; whether or not this is the case can be tested in the following manner. The concentration of the hydrogen chloride in the mixture is $n(1-X)/2v$, that of the methyl ether $n(1-X)/2v$, and that of the oxonium compound $nX/2v$; hence, if the above equilibrium between oxonium compound, methyl ether and hydrogen chloride really exists,

$$\frac{n\ (1-X)^2}{2vX} = K \qquad (2)$$

where K is a constant

Substituting $\frac{Pv}{RT}$ for n

$$\frac{P(1-X)^2}{X} = 2\ RTK = k \qquad (3)$$

where k is a constant at a definite temperature.

Hence X and consequently p (Eq. 1) can be calculated for various value of P and this value checked by experiment.

TABLE II

EXPERIMENTAL DATA AND CALCULATED AND OBSERVED VALVES OF p

Temp. °C.	Press. HCl P_1 mm.	Press. $(CH_3)_2O$· P_2 mm.	X Calc.	Press. of mixt. Calc. p mm.	Press. of mixt. Found	Difference
18.8	756.0	756.0	0.1124	...	713.53	...
	573.4	573.4	.0896	547.8	547.5	+0.3
	382.9	382.9	.0634	368.8	369.2	−0.4
9.2	758.0	758.0	.1472	...	702.2	...
	557.0	557.0	.1162	524.7	524.4	+0.3
	378.7	378.7	.0848	362.65	362.7	−0.05
	218.4	218.4	.0524	212.7	212.5	+0.2
	767.8	385.5	...	546.1	545.2	+0.9
	382.1	758.5	...	540.2	539.8	+0.4

The first experiments carried out at 18.8° show agreement within experimental error between calculated values and those found. The calculation was based on the value of k at 18.8° and atmospheric pressure. See Table I.

Furthermore, the test of varying the relative proportions of the gases to be mixed was applied. In this case p can be calculated as follows.

Let P_1 equal the pressure of unmixed hydrogen chloride of which there are N_1 gram molecules in volume v; let P_2 be the pressure of unmixed methyl ether of which there are N_2 gram molecules in volume v.

Then, if N_3 gram molecules of oxonium compound are formed.

$$\frac{\frac{(N_1-N_3)}{(2v)}\ \frac{(N_2-N_3)}{(2v)}}{\frac{N_3}{2v}} = K \qquad (4)$$

where K is identical with K in Equation 2.

$$N_1 = \frac{P_1v}{RT} \qquad N_2 = \frac{P_2v}{RT}$$

$$(N_1 + N_2 - N_3) = \frac{2pv}{RT}$$

$$\therefore N_3 = \frac{P_1v}{RT} + \frac{P_2v}{RT} - \frac{2pv}{RT}$$

and substituting for N_1 N_2 N_3 in Equation 4,

$$\frac{(2p-P_2)(2p-P_1)}{(P_1 + P_2 - 2p)} = 2RTK = k \tag{5}$$

The next series of experiments was carried out at 9.2°. The pressure change on mixing the gases (56.0 mm.) is greater than at the higher temperature and, therefore, the experimental error is correspondingly smaller. The very good agreement between calculated and observed values shows that the assumption of the equilibrium in which there is a 1:1 compound is without doubt correct[6] and the result is not due to the mass effect of changed molecular attraction in the gas mixture.

As was mentioned above, at temperatures below —4°, the condensation temperature (boiling point) of the mixture being near, the molecular attractions play a part as well as association in causing a diminution in pressure when the gases are mixed. At —7.65° the above calculation should, therefore, not be valid because the association X is really smaller than that calculated from the diminution of pressure, and hence the diminution calculated on this basis for a lower pressure of unmixed gases will be smaller than that observed. An experiment was carried out at this temperature in which the original pressures of hydrogen chloride and methyl ether were 383.2 mm. of mercury. The pressure observed on mixing was 363.0 mm., whereas that calculated on a basis neglecting molecular attraction was 331.5.

The conclusion which may be drawn from all of these experiments is that methyl ether and hydrogen chloride form an oxonium compound, $(CH_3)_2O.HCl$, existing in the vapor state to a measurable extent even at temperatures 150° above its melting point. The compound is quite analogous to ammonium chloride which also is partly dissociated into its component molecules when it is vaporized.[7]

In the latter case, 2 polar molecules form the resultant compound. Methyl ether is not polar, that is, in the sense that the center of gravity of the positive and negative electricity is identical when the molecule is built up out of atoms to which the Langmuir or Thomson electron structure is given. Although this is in agreement with its dielectric constant, the

[6] At 9.2° and 758.0 mm. pressure the decrease in pressure on mixing is 55.8 mm. Hence, at half the initial pressure, 378.7 mm., one might have expected half the above decrease in pressure 27.9 mm., but the decrease in pressure found was 16.0 mm. which is in perfect agreement with the calculated change (See Table II).

[7] Smith and Lombard, THIS JOURNAL, **37**, 38 (1915).

stability of the oxonium compound is rather surprising. However, from the space model it can be imagined that the approach of the hydrogen end of the very polar hydrogen chloride molecule to the oxygen of the methyl ether might induce pronounced polarity in the latter. This would mean a displacement of the methyl groups and the attachment of a hydrogen nucleus to the oxygen atom quite in agreement with the electrolytic dissociation of the oxonium compound when in solution. Furthermore, the oxonium compound itself would be polar, which would account for the higher complexes[2] $[(CH_3)_2O.3HCl]$ which have been isolated at low temperatures.

It will be interesting to investigate other oxonium compounds in this manner. The compound formed between ether and chlorine is particularly interesting, since in this case neither of the component molecules is itself polar in the above sense. This compound, therefore, should not be detectable in the gaseous state.

In this connection it may be pointed out that the chlorine complexes when melted are non-conductors, that is, no electrolytic dissociation occurs.

The heat of formation of methyl ether-hydrogen chloride can be calculated from the above experimental data, but this will be left until other oxonium compounds have been examined.

Acknowledgment is hereby made of a scholarship granted during the time of this research by the Honorary Advisory Council for Scientific and Industrial Research of Canada.

Summary

Equal volumes of methyl ether and hydrogen chloride were mixed in the gaseous state at atmospheric pressure and the resultant pressures recorded over the temperature range 30° to —10°. From these data the amount associated to form the oxonium compound, $(CH_3)_2OHCl$, was calculated, and the resultant pressures on mixing these gases, at pressures other than atmospheric and in unequal proportions, were deduced. These latter were checked by observation, thus proving the original assumption to be correct, namely, that a 1 : 1 compound exists in the vapor state, the dissociation of which increases with rising temperature.

The similarity between methyl ether-hydrogen chloride and ammonium chloride has been pointed out and the formation of the former attributed to induced polarity in the methyl ether molecule caused by the polar hydrogen chloride molecule.

MONTREAL, CANADA