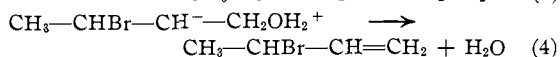has been interpreted in terms of resonance between the structures $CH_3—CH=CH—CH_2^+$ and $CH_3—CH^+—CH=CH_2$. If such ions are coordinated with solvent molecules, obviously the possibility of resonance disappears. The following alternative mechanism is entirely in accord with the considerations advanced above

$CH_3—CH=CH—CH_2OH + HBr \longrightarrow$
$\qquad CH_3CH=CH—CH_2OH_2^+ + Br^-$ (1)
$CH_3—CH=CH—CH_2OH_2^+ + Br^- \longrightarrow$
$\qquad CH_3—CH=CH—CH_2Br + H_2O$ (2)
$CH_3—CH=CH—CH_2OH_2^+ + Br^- \longrightarrow$
$\qquad CH_3—CHBr—CH^-—CH_2OH_2^+$ (3)
$CH_3—CHBr—CH^-—CH_2OH_2^+ \longrightarrow$
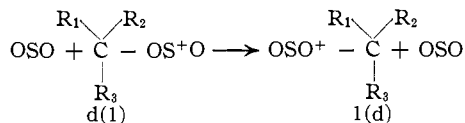$\qquad CH_3—CHBr—CH=CH_2 + H_2O$ (4)
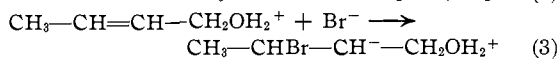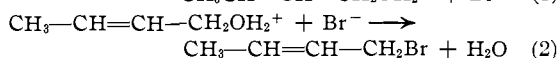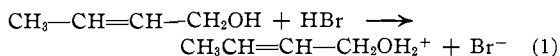
and similarly for methylvinylcarbinol. It should be noted that reaction (2) (of the usual type accompanied by Walden inversion) gives the normal product, while reactions (3) and (4) yield the rearranged product. Reactions (3) and (4) are similar to those previously postulated to explain the addition of halogens to ethylene linkages.[13]

The various cases in which rapid racemization of optically active carbonium ions has been noted[14] are explicable in terms of an identical exchange reaction of the coördinated ion with the solvent molecules, as, say, in liquid sulfur dioxide.

(13) R. A. Ogg, Jr., THIS JOURNAL, 57, 2727 (1935).
(14) E. S. Wallis and F. H. Adams, ibid., 55, 3838 (1933); E. Bergmann and M. Polanyi, Naturwissenschaften, 21, 378 (1933).

$$OSO + \underset{\underset{d(l)}{\overset{|}{R_3}}}{\overset{R_1\diagdown\;\diagup R_2}{C}} - OS^+O \longrightarrow OSO^+ - \underset{\underset{l(d)}{\overset{|}{R_3}}}{\overset{R_1\diagdown\;\diagup R_2}{C}} + OSO$$

The above two examples are typical. It seems legitimate to state that it is never necessary to assume the existence of carbonium ions with an open sextet as intermediates in organic reactions, and that in view of the considerations of reaction energetics advanced above, preference is to be given to mechanisms not involving such ions.

Summary

It is shown that dissociation of a methyl halide (in aqueous solution) into a methyl ion with an "open sextet" and a halide ion is endothermic by at least some 50 kcal. per mole, and more probably by some 70 kcal. On the other hand, reaction with water to yield halide ion and the coördinated methyl ion $CH_3OH_2^+$ is practically thermoneutral. Comparison with the experimental data for methyl halide hydrolysis leads to rejection of the Hughes–Ingold mechanism (involving CH_3^+) in favor of the Olson–Halford mechanism (involving $CH_3OH_2^+$).

It is suggested that carbonium ions with an open sextet never play an appreciable role in observable organic reactions, and that mechanisms employing such ions must be abandoned.

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE UNIVERSITY OF IOWA]

Physical Studies of Non-aqueous Solvates. III. The Vapor Pressure of Zinc Bromide–Diethyl Ether Solutions

BY H. H. ROWLEY AND FLORENCE V. OLSON[1]

Considerable work has been reported on the preparation and properties of magnesium bromide–diethyl ether systems.[2–4] Extension of the investigation of non-aqueous solvates would naturally include systems resembling the one already mentioned. The zinc bromide–diethyl ether system was chosen for this investigation since zinc belongs to the same periodic group as magnesium

and the formulas of the compounds of the two metals are similar. Further, zinc, like magnesium, adds to alkyl halides in an ether medium to form organo-metallic compounds.

One of the first to report in the literature on zinc bromide diethyl etherates was Nickles,[5] who found them to be quite unstable. Raynaud[6] later prepared zinc bromide, using Nickles' method. The two layer system first formed, the lower layer of which was reddish in color, disappeared on further addition of bromine to give a homogeneous, brownish-violet liquid. Removal of excess ether left a

(1) Present address: Women's College of the University of North Carolina, Greensboro, N. C.
(2) B. N. Menschutkin, Z. anorg. Chem., 49, 34 (1906).
(3) J. Meisenheimer and J. Casper, Ber., 54B, 1655 (1921); J. Meisenheimer, E. Piper and H. Lange, Z. anorg. allgem. Chem., 147, 331 (1925).
(4) (a) W. V. Evans and H. H. Rowley, THIS JOURNAL, 52, 3523 (1930); (b) H. H. Rowley, ibid., 58, 1337 (1936); (c) H. H. Rowley, ibid., 59, 621 (1937).

(5) M. J. Nickles, Compt. rend., 52, 396, 869 (1861).
(6) A. Raynaud, Bull. soc. chim., 39, 195 (1926).

black liquid stable at 110°, which on analysis corresponded to $ZnBr_2 \cdot (C_2H_5)_2O$. Raynaud claimed verification of this monoetherate by preparing it in a different manner. Sublimed zinc bromide was dissolved in ether and the excess ether removed by heating on a water-bath. The resulting viscous solution was allowed to crystallize in a desiccator containing tallow and concentrated sulfuric acid. Analysis of the solid gave percentages that corresponded to those calculated for the monoetherate.

To check these results and establish other possible diethyl etherates of zinc bromide as well as to learn something of their stability, the vapor pressures of saturated solutions of zinc bromide–diethyl ether solutions were measured over the temperature range −10 to +35°. The wet solids in contact with the saturated solutions were also analyzed at certain temperatures.

Experimental

Apparatus and Materials.—The vapor pressures were measured by the static method using the same apparatus and technique described in a previous paper.[4c] The diethyl ether was of reagent grade, dried, distilled and kept over freshly cut sodium, only the middle third fraction of the distillate being used.

At first, an attempt was made to prepare the solution of zinc bromide in ether by Nickles' method,[5] which was to treat pure zinc turnings in ethyl ether with liquid bromine, cooling when necessary to avoid too violent a reaction. But instead of a colorless two-layer system, like that of magnesium bromide in ether,[2] a yellowish colored two-layer system was first formed, which upon further addition of bromine became a homogeneous purplish-black liquid, as was described by Raynaud.[6]

Another method tried was that of treating a solution of dry hydrogen bromide in ether with zinc turnings. Hydrogen was evolved, and after a short interval a colorless, partially immiscible liquid phase appeared which lasted only as long as the solution was saturated with hydrogen bromide. No solid was precipitated at room temperature from solutions thus prepared.

The method finally used in preparing the solutions was that of adding pure anhydrous zinc bromide to dry ether until a fairly concentrated solution was obtained. The solid zinc bromide was obtained by subliming the C. P. anhydrous product (Baker Analyzed) in a specially constructed Pyrex vessel. During the sublimation and in all subsequent handling of the solutions, the work was carried out in an atmosphere of dry carbon dioxide.

Procedure.—The unsaturated solution, at room temperature, was transferred to the vapor pressure flask, cooled to −78° in carbon dioxide–acetone bath, quickly sealed to the apparatus and evacuated at that temperature with a good oil pump for about thirty minutes. The mercury was then raised in the differential manometer, cutting off the sample flask from the vacuum system, and the sample raised to a sufficiently high temperature to dissolve the solid which was precipitated at the low temperature.

The sample was again cooled to −78° and the space above evacuated. In this way, occluded gases could be removed from the sample.

Before readings on the differential manometer were taken, the flask was kept at the desired temperature for several hours, if a solid phase were present at that temperature. If the solution were unsaturated at the desired temperature, known amounts of ether were distilled from the sample until it did contain a solid phase under the conditions desired. Since the solid phases seldom formed of themselves, because of suspended transformation, in order to obtain the stable solid phases it was necessary to cool the samples to fairly low temperatures and then bring them to the desired temperature range and allow them to come to equilibrium.

It was found that a sample which contained considerable solid at 0° might be unsaturated at higher temperatures. Thus as the temperature was raised it was necessary to reduce the amount of ether in the sample. The excess ether was condensed in a calibrated reservoir and the volume recorded. At the end of the measurements all the ether was distilled from the sample into the reservoir, the sample flask was filled with dry air, cut off, and weighed. It was then cleaned, dried and weighed again, and the weight of the pure zinc bromide determined. From the volume and the density of ether at 25°, the moles of ether could be calculated and the mole ratio of diethyl ether to zinc bromide determined for any series of measurements.

The approximate composition of the stable solid phase in equilibrium with the saturated solution at a definite temperature, was determined in the following manner. Saturated solutions were prepared in small flasks, allowed to come to equilibrium and the supernatant solution was poured off quickly. Keeping the temperature as nearly constant as possible, the wet solid was drained for a few minutes, then a sample was weighed, dissolved in water and the total bromide concentration determined gravimetrically as silver bromide.

To check the results of Raynaud,[6] solutions saturated at room temperature were decanted into small evaporating dishes, which were placed in a desiccator containing lard and concentrated sulfuric acid for the adsorption of ether vapor. After a few days, a solid was precipitated, samples of which were taken and analyzed in the manner just described.

Discussion of Results

The vapor pressure study of this system presented difficulties due to the high solubility of zinc bromide in diethyl ether giving rise to viscous, sluggish solutions. Unsaturated solutions at +25°, which would normally contain solid at +15°, could be cooled to 0° and left there for an indefinite time without crystallization occurring. An example of this suspended transformation is shown in Fig. 1, where the logarithm of the vapor pressure is plotted against the corresponding reciprocal absolute temperature. The continuous line at the left in the graph is for the system liquid–
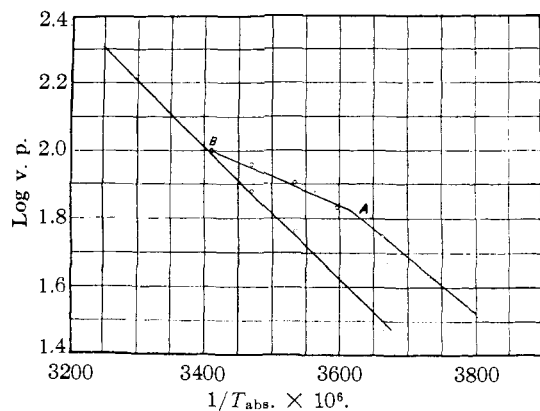
Fig. 1.

vapor, containing no solid. Above point B it represents an unsaturated solution, below B, a supersaturated solution. The other two lines represent the same system when stable solid phases were present with the liquid and vapor phases.

TABLE I

CHANGE OF VAPOR PRESSURE WITH TEMPERATURE FOR THE SYSTEM ZINC BROMIDE–DIETHYL ETHER

Temp. of bath, °C.	$1/T_{abs.}$ $\times 10^6$	Vapor press., mm.	No. of samples	Log v. p.
−10	3802	34 ± 1	4	1.5315
− 5	3731	41 ± 2	4	1.6128
0	3663	57 ± 2	7	1.7559
+ 5	3597	70 ± 4	4	1.8451
10	3534	79 ± 4	4	1.8976
15	3472	89 ± 4	4	1.9494
20	3413	101 ± 2	4	2.0043
25	3356	118 ± 3	5	2.0719
30	3300	156 ± 1	2	2.1931
35	3247	192 ± 1	2	2.2833

Table I lists the data graphed in Fig. 2 for systems of zinc bromide–diethyl ether in which there was a solid, liquid and vapor phase present for the temperature range −10 to +35°. The extreme slowness with which the system attained equilibrium and the persistence of the metastable phases made it difficult to obtain precise vapor pressure measurements. It is to be noted in both Fig. 1 and Fig. 2 that there is a definite change of slope at points A and B. The first break, at point A in both graphs, occurs between 0 and 5°, and the second, at point B, in the neighborhood of 20°. These changes in slope would indicate a change in the nature of the solid phase in equilibrium with the solution. Since there are three sections to the curve, it might be assumed that three distinct solid phases are present in the temperature interval −10 to +35°, the first stable up to about 5°,

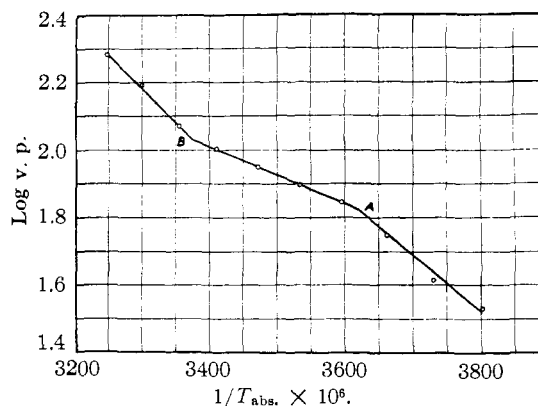the second between 5 and 20° and the third stable above 20°.

Fig. 2.

These changes in the solid phases could be seen directly. The solid in equilibrium with the saturated solution at 0° crystallized in transparent plates. Between 0 and 5° these disappeared and the solid in equilibrium at 15° was composed of transparent needles. At 25° and above the equilibrium solid was opaque and finely divided so that no crystalline shape was evident.

In order to establish the composition of the solid phase in equilibrium with the solution, samples were analyzed as described. Due to the unstability of the solids and viscosity of the solutions, it was not possible to remove all of the occluded liquid. Hence the "wet solids" were analyzed in an effort to obtain an approximate composition. The results of these analyses at 0, 15 and 25° are summarized in Table II.

TABLE II

ANALYSIS OF "WET SOLIDS" IN EQUILIBRIUM WITH SOLUTIONS

Temp., °C.	No. of samples analyzed	Wt. % ZnBr₂
0	5	58.7 ± 0.6
15	3	70.7 ± 0.5
25	6	85.6 ± 1.4

Determinations of zinc bromide in the wet solid at 0° always gave values around 59 wt. %. The theoretical value of zinc bromide in the dietherate, $ZnBr_2 \cdot 2(C_2H_5)_2O$, is 60.3% and that in the trietherate, $ZnBr_2 \cdot 3(C_2H_5)_2O$, is 50.3 wt. %. The value for the zinc bromide in the solid will be lower than that in the pure etherate because the solid was always wet with solution, which contains only 55–57 wt. % of zinc bromide at 0°. Therefore, it can be concluded that the solvate in equilibrium with the solution at 0° is the dietherate.

Likewise, the average value of 70.7 wt. % for the determination of zinc bromide in the solid, stable in contact with the saturated solution at 15°, agrees favorably with the theoretical value, 75.3, of the weight per cent. of zinc bromide in the monoetherate, $ZnBr_2 \cdot (C_2H_5)_2O$. The solubility of zinc bromide at 15° is approximately 68–69 wt. %.

Analyses of the wet solid, stable in contact with the saturated solution at 25°, would vary somewhat according to the extent to which the viscous solution was drained from the solid. The average value of 85.6% indicates that the monoetherate is not stable at this temperature. The solubility of zinc bromide at 25° is approximately 69–70 wt. %.

From these results, it would appear that the transition in the solid phase in the range 0 to 5° is that of the dietherate of zinc bromide to the monoetherate, and the transition of the solid phase in the neighborhood of 20° is that of the monoetherate to the unsolvated zinc bromide.

The results of this investigation do not agree with those of Raynaud.[6] He stated that the solubility of zinc bromide in diethyl ether at 25° was about 45 wt. %; the value found in this work is 69–70 wt. %. He stated further that the monoetherate is stable at room temperature. Part of his work was repeated in this Laboratory and the wet solid formed by allowing a solution to evaporate in a desiccator gave an average value of 86.7 wt. % zinc bromide. With a specially well drained sample this value rose to 90%. The indications in the present work are that the monoetherate, in contact with solution, decomposes in the neighborhood of 20°.

Several possible sources of error may be pointed out in Raynaud's work. As was found in the present study, bromination of zinc in diethyl ether led to the formation of a dark homogeneous liquid. To conclude that this was a pure solution of zinc bromide in ether or to draw any conclusions on the existence of the monoetherate from analysis of this dark liquid certainly was not justifiable. In the present study, a dark liquid was not obtained at any time when pure zinc bromide was dissolved in ether. A further criticism of Raynaud's work is that he mentioned taking no special precautions to exclude moisture in the dissolving of solid zinc bromide in ether. Since zinc bromide hydrolyzes in water, the presence of moisture may have caused the variations in the analyses of the solutions and in the analyses of the solid obtained by allowing the solution to evaporate in a desiccator.

Summary

1. A study of the vapor pressures of the system zinc bromide–diethyl ether over the temperature range -10 to $+35°$ has been made.

2. The existence of the two etherates, the dietherate of zinc bromide, $ZnBr_2 \cdot 2(C_2H_5)_2O$, and the monoetherate, $ZnBr_2 \cdot (C_2H_5)_2O$, has been indicated by (a) breaks occurring between 0 and 5° and in the neighborhood of 20° in the curve obtained by plotting the logarithms of the vapor pressures of the system against the reciprocal of the absolute temperature; (b) analyses of the wet solids in contact with the saturated solutions at 0, 15 and 25°; (c) changes in the appearance of the solids in the ranges 0 to 5° and in the neighborhood of 20°.

3. Disagreements with Raynaud on the system zinc bromide–diethyl ether have been mentioned, and possible sources of error in his work indicated.