Benzoate of 7-Hydroxycholesteryl Chloride.—A solution of 22.6 g. of 7-hydroxycholesteryl chloride in 150 cc. of dry pyridine was cooled in ice and 50 cc. of benzoyl chloride was added in small portions with shaking. The solution was allowed to stand at room temperature for two days after which it was poured into 4 liters of water and allowed to stand overnight. The water was decanted and the residue dissolved in ether, the ether solution being washed with sodium carbonate solution after which it was concentrated to 100 cc. and 200 cc. of methyl alcohol added. After standing overnight, crystals formed which were recrystallized from acetone. The yield was 11 g. and the melting point 119°.

Anal. Calcd. for $C_{34}H_{49}O_2Cl$: C, 77.9; H, 9.4. Found: C, 78.2; H, 9.6.

Summary

epi-Cholesterol was prepared from the hydrolysis of 7-keto-cholesteryl chloride with potassium acetate followed by reduction of the ketone group by the Wolff-Kishner method. Catalytic reduction by platinum oxide in acetic acid of either 7-keto-cholesteryl chloride or 7-hydroxycholesteryl chloride gave a mixture of cholestyl chloride and 7-hydroxycholestyl chloride. Derivatives of the various products were prepared.

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Physical Studies of Non-aqueous Solvates. II. The Vapor Pressure of Magnesium Bromide-Diethyl Ether Solutions

BY H. H. ROWLEY[1]

The vapor pressure of an ethyl ether solution saturated with magnesium bromide was reported by Evans and Rowley[2] to be 410 mm. at +25°. Scherer and Newton,[3] using the vapor pressure values of magnesium bromide-ethyl ether systems to calculate the free energy of formation of magnesium bromide, also reported a value of 410 mm. at +25° for a solution of ether saturated with magnesium bromide. It is a well established fact[2,4] that magnesium bromide with excess ethyl ether forms two conjugate liquid phases at +25°, the upper layer consisting of ether saturated with magnesium bromide (3.23 g./100 g. Et_2O), the bottom layer containing about 39% magnesium bromide. Re-examination of the data of Evans and Rowley indicated that under the conditions of the experiment the only liquid present was the oily bottom layer containing about 39% magnesium bromide and absolutely none of the light upper layer. Thus, the vapor pressure reported was not for an ethyl ether solution saturated with magnesium bromide.

In order to prove this, the vapor pressure of the two conjugate liquid phases has now been measured over a temperature range from 0 to +25°. The system also has been studied in more detail at +25° varying the ratio of $MgBr_2:Et_2O$ from $^1/_4$ to 1.

Experimental

Apparatus.—The vapor pressures were measured by the static method as shown in Fig. 1. The samples were placed in a flat-bottomed flask (A), about 4 cm. in diameter and 5 cm. in height, sealed to a Pyrex spiral (B) about 4 cm. in diameter and 16 cm. in length, connected to a mercury U-manometer (C). The flexible glass spiral together with the relatively large surface of the sample, allowed the sample to be agitated vigorously by gently tapping the flask (A). Thus, thorough mixing and equilibrium conditions were attained rapidly. The mercury in the manometer (C) could be raised or lowered by adjusting the pressure in reservoir (D) and served also to seal the sample from the rest of the system and protect it from stopcock grease. When it was necessary to evacuate the space above the sample, the mercury was lowered and the sample

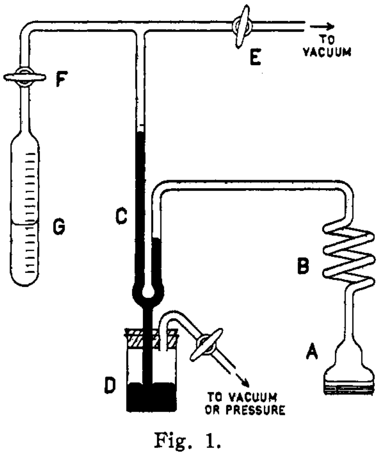

Fig. 1.

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(1) Department of Chemistry, State University of Iowa, Iowa City, Iowa.

(2) W. V. Evans and H. H. Rowley, THIS JOURNAL, **52**, 3523 (1930).

(3) Geo. A. Scherer and Roy F. Newton, *ibid.*, **56**, 18 (1934).

(4) (a) H. H. Rowley, *ibid.*, **58**, 1337 (1936); (b) B. N. Menschutkin, *Z. anorg. Chem.*, **49**, 34 (1906).

connected directly to a Cenco Hy-Vac pump (protected from ether vapor by activated charcoal at −78°) through stopcock (E). During the measurements, stopcock (E) was always connected to the vacuum pump so the vapor pressure values could be read directly on the manometer (C). All the connecting tubes were of 8-mm. Pyrex glass.

Dry, distilled ether was stored in tube (G) sealed to the system and cut off by stopcock (F). Thus, ether could easily be distilled from or added to the sample by lowering the mercury in (C) and immersing the ether tube (G) or the sample flask (A) in a mixture of carbon dioxide and acetone. The ether reservoir was calibrated in 0.5 cc. and the volume could be read to less than 0.2 cc.

This type of apparatus had the advantage of a relatively small volume above the sample, very little of it outside the bath and no stopcocks or joints in contact with the ether vapor whose pressure was being measured. The room temperature was always kept above +25° during the measurements to prevent any condensation of ether vapor when the sample was at +25°.

Procedure.—The magnesium bromide–ethyl ether solution was prepared in an Erlenmeyer flask, taking the usual precautions against moisture and light.[4a] The two-layer system was transferred to a dry sample flask, cooled to −78° in a carbon dioxide–acetone mixture and sealed to the apparatus. The apparatus was evacuated for about thirty minutes with the sample at −78°. The mercury was then raised in the U-manometer and the sample brought to +25° and agitated until it was completely liquid again. The first measurements made at +25° were invariably high due to occluded gases which were released on melting the sample. To remove these, the sample was again cooled to −78°, where the normal vapor pressure is about 0.6 mm. and the "occluded" gases, which did not condense, pumped off. Generally, one such treatment was sufficient to remove these gases and the vapor pressure of the system would give reproducible values at a constant temperature.

Ether was distilled from the sample at intervals and condensed in the reservoir (Fig. 1, G) and its volume measured at +25°. From this value and the density of ether at +25°, the grams and hence the moles of ether distilled could be calculated. When all the ether had been distilled from the sample and the experiment completed, the sample flask was filled with dry air, cut off and weighed. It was then cleaned and weighed again and the weight of anhydrous magnesium bromide determined. From these data, the mole ratio of magnesium bromide to ethyl ether could be calculated for any series of measurements. Some experiments also were made by desolvating the sample and weighing before sealing to the apparatus. Known amounts of ether were then distilled onto the sample and measurements made.

The flasks were kept at constant temperature by means of water-baths in vacuum flasks. At 0° the melting point of ice was used. The 0.1° thermometers were calibrated at 0° and at the transition point of sodium sulfate decahydrate. The temperature measurements were accurate to ±0.03°. The manometer readings were corrected to 0° by values obtained from the "International Critical Tables"[5] and were accurate to ±0.5 mm.

Results.—The values for the vapor pressures of ethyl ether solutions saturated with magnesium bromide between 0 and +25° are shown in Table *I*. *In all* cases there was excess ether present. The equilibrium phase at temperatures below 12° is solid magnesium bromide triethyl etherate, between 12 and 22.5° it is the solid diethyl etherate, and above 22.5° the immiscible liquid containing about 39% magnesium bromide.[4a] The vapor pressure for dry redistilled ethyl ether determined in the same apparatus is also included in Table I for comparison. The values for the vapor pressure lowering shown in column 4 were measured directly by connecting one side of the manometer to the ether reservoir at the same temperature as the sample. These readings were made with a Cenco Comparator accurate to ±0.1 mm.

TABLE I

VAPOR PRESSURE OF ETHYL ETHER SOLUTIONS SATURATED WITH MAGNESIUM BROMIDE

Temp., °C.	V. p. of Et_2O, mm.	V. p. of satd. soln., mm.	ΔP[a] mm.
0	186.7 ± 0.1	185.7 ± 0.1	1.1
5	234 ± 0.5	233 ± 0.5	
10	292	290	
15	361	359	2.1
20	442	438	
25	537	532	5.1

[a] Values in col. 4 were measured directly on a differential manometer with an accuracy of ±0.1 mm.

A series of experiments also was run at 25° in which the ratio of ethyl ether to magnesium bromide was varied. Whenever sufficient ether was present to form two conjugate liquid phases, the value for the vapor pressure of the system was always 532 mm. at +25°. However, as the ether was removed from the sample at 25°, the light upper layer became smaller and finally disappeared. At this point, the vapor pressure of the system began to decrease as the ratio of ether to magnesium bromide was lowered, fairly rapidly if only one liquid phase was present but not so rapidly if two phases, liquid and crystal, appeared. As the mole ratio of magnesium bromide to ethyl ether approached 1:2.0, the values dropped off very rapidly until they were about 390 mm. when all the liquid phase had disappeared and only crystals remained. This value for the vapor pressure of magnesium bromide diethyl etherate in equilibrium with the monoethyl etherate remained constant from a mole ratio of 1:2.0 to 1:1.0. The results of a group of measurements are shown in Table II.

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(5) "International Critical Tables," Vol. I, 1928, pp. 68–69.

TABLE II

CHANGE OF VAPOR PRESSURE AT +25° WITH MOLE RATIO

Mole ratio $MgBr_2 : Et_2O$	Vapor press. immiscible layer, mm.	Vapor press. immiscible layer with crystals, mm.	Vapor press. crystals, mm.
1:3.69	529		
1:3.58	523.5		
1:3.48	518.5		
1:3.32	511.5		
1:3.16	501.5		
1:3.05	481.5		
1:2.85	449.5	499.5	
1:2.64		502.5	
1:2.64		498.5	
1:2.58	397.5	492.5	
1:2.48		483.5	
1:2.38		498.5	
1:2.36		494.5	
1:2.32		480.5	
1:2.24		489.5	
1:2.00+		404	
1:1.99			389
1:1.92			392
1:1.86			385.5
1:1.84			389.5
1:1.28			392

TABLE III

EFFECT OF MOISTURE ON VAPOR PRESSURE AT +25°

Mole ratio $MgBr_2: Et_2O$	Mole ratio $MgBr_2: H_2O$ (estimated)	Vapor press. immiscible layer, mm.	Vapor press. immiscible layer with crystals, mm.	Vapor press., crystals, mm.
1:3.96	1:0.05	530.5		
1:3.83	1:0.05	528		
1:3.70	1:0.05	523		
1:3.48	1:0.05	510.5		
1:3.34	1:0.05	501		
1:3.21	1:0.05	483.5		
1:2.95	1:0.05	448	467.5	
1:2.69	1:0.05		448.5	
1:2.65	1:0.2		447	
1:2.55	1:0.05		421	
1:2.42	1:0.2		412	
1:2.36	1:0.2		402	
1:2.12	1:0.2		398	
1:2.06	1:0.2		388.5	
1:1.98	1:0.05			387.5
1:1.53	1:0.2			360.5
1:1.50	1:0.05			368.5
1:1.18	1:0.2			327.5

Effect of Moisture.—Inasmuch as the presence of moisture is known to affect the apparent solubility of magnesium bromide in ethyl ether,[4a] several experiments were performed to determine its effect on the vapor pressure of the solutions. The solutions were made in the usual manner and placed in the sample flask. Before sealing to the apparatus, measured amounts of distilled water were added to the samples. In every case, a white precipitate formed at first but redissolved on agitation. The "moist" samples gave the appearance of being perfectly normal.

The measurements were made in exactly the same manner as for a dry sample. The results are shown in Table III. The vapor pressure of a "moist" two-layer system containing excess ether was found to be 531.5 mm. at 25° as compared to 532 mm. for the dry samples. After the disappearance of the light upper layer, the vapor pressure of the system decreased with decreasing amounts of ether as was found with a normal sample. However, for corresponding mole ratios, the values for the "moist" sample were always below those for the normal samples, being 50 to 100 mm. lower when the mole ratio was between 1:3.0 and 1:2.0.

Effect of Age.—The effect of the age of the sample on the vapor pressure was measured on one sample that had been sealed in a glass tube for over three months at +25°. The upper ether layer was colorless but the heavy immiscible layer had become a dark brown. The vapor pressure of the two layer systems at +25° was 531.5 mm. compared to 532 mm. for a fresh sample. The heavy immiscible layer gave values about 20 to 25 mm. below those for a fresh sample of corresponding composition. Whether this was due to some change in the solution (mixture had darkened with age) or to possible presence of moisture could not be determined.

Discussion

The values for the vapor pressures of ethyl ether solutions saturated with magnesium bromide as shown in Table I are only a few millimeters below those for pure ether. The lowering at 0° is 1.1 mm.; at +15°, 2.1 mm.; and at +25°, 5.1 mm.; the solubility of magnesium bromide at these temperatures is, respectively, 0.70 g., 1.72 g., 3.23 g./100 g. ethyl ether.[4a] Assuming the applicability of Raoult's law to solutions of these concentrations, the molecular weight of dissolved magnesium bromide (mol. wt. 184.2) as calculated is 88 at 0°, 220 at +15° and 252 at +25°. This apparent increase in molecular weight with increasing concentration is in agreement with the results of Meisenheimer and Schlichenmaier,[6] who studied the boiling point rise of ethyl ether solutions of ethylmagnesium bromide and magnesium iodide. However, too much stress should not be

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(6) Jakob Meisenheimer and Walter Schlichenmaier, *Ber.*, **61B**, 720 (1928).

placed on this apparent increase in molecular weight since it is highly probable that Raoult's law is not valid for this type of solution. The fact that these compounds form known solid solvates with ethyl ether and two of them form two conjugate liquid phases at room temperature, indicates that the solutions would not be ideal.

It should be noted that the vapor pressure of pure diethyl ether at 0° as recorded in this work is 186.7 ± 0.1 mm. compared to 185.3 mm. as given in the "International Critical Tables."[7] This value was checked with many carefully purified samples and with several modifications of the apparatus. The values obtained between +10 and +25° agree within the experimental error with the literature values.

Since the vapor pressure of the ethyl ether–magnesium bromide system was always constant at +25° if the mole ratio of magnesium bromide to ether was greater than 1:4.00, it appears justified to call 532 mm. the vapor pressure of a solution of ethyl ether saturated with magnesium bromide. Reference to the solid line in Fig. 2 and to Table II shows that when the mole ratio falls below 1:3.8, the two-layer system disappears leaving only the heavy bottom layer. As the mole ratio is decreased, the vapor pressure of the system falls rapidly along the line ABC as long as only one liquid phase is present. However, the portion of the curve BC appears to be metastable, for if a crystal phase appears the vapor pressure rises to a value on the curve BD. Thus, between the mole ratios 1:3.3 and 1:2.0, the three phase system: magnesium bromide dietherate crystals—a concentrated solution of magnesium bromide in ethyl ether–ether vapor, is stable. As the ether is removed from the system, the liquid phase diminishes with a correspondingly slight decrease in vapor pressure except as the system approaches a mole ratio of one magnesium bromide to two ethyl ethers. At this point (E) the liquid phase disappears, leaving the crystals of magnesium bromide diethyl etherate. Further removal of ether does not change the vapor pressure of the system magnesium bromide dietherate–magnesium bromide monoetherate–ether vapor until the mole ratio has dropped to 1:1.

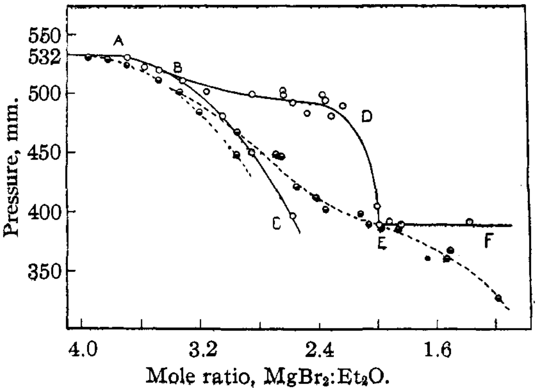

Fig. 2.—○, Dry sample; ⊖, "Moist" sample.

The presence of moisture is shown to have a decided effect on the vapor pressure of the system as indicated in Table III and Fig. 2. Above a mole ratio of 1:4.0, the values for a "moist" sample are about 0.5 mm. below those for a normal sample. Below a mole ratio of 1:4.0 the vapor pressure of the liquid phase parallels that of a dry sample but is consistently below it as shown by the broken line in Fig. 2. The appearance of a crystal phase raises the values somewhat but they are considerably below those for a normal sample of the same composition. It is interesting to note that below a mole ratio of 1:2.0, the vapor pressure of the "moist" sample does not appear to remain constant. This might be due to slow equilibrium, though several of the values showed no increase after twenty-four hours.

The present work appears to show that the vapor pressure of an ethyl ether solution saturated with magnesium bromide is not 410 mm. at +25° as reported by Evans and Rowley[2] and Scherer and Newton[3] but is 532 mm. In the case of Evans and Rowley, it is definitely known that under the conditions of the experiment, the mole ratio of the system measured was below 1:3.0 and that there was the possibility of a trace of moisture being present. Reference to Fig. 2 shows that under these conditions it would be very possible to obtain a value such as was reported. It is likewise probable that Scherer and Newton[3] encountered the same difficulty.

Summary

1. The vapor pressure of diethyl ether saturated with magnesium bromide has been measured over the temperature range from 0 to +25°, and in more detail at 25° with variations in the ratio between magnesium bromide and ether from $^1/_4$ to 1.

2. The presence of small amounts of moisture

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[7] "International Critical Tables," Vol. III, 1928, p. 219.

was found to alter greatly the vapor pressure of the magnesium bromide–ethyl ether system. This fact was advanced as a possible explanation for the low values reported in the literature by several authors.

EVANSTON, ILL. RECEIVED JANUARY 2, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Effect of Iodine on the Rates of Decomposition of Formaldehyde, Acetaldehyde and Propionaldehyde

BY G. K. ROLLEFSON AND R. FRANCIS FAULL

In a previous note[1] we have presented data which show that the accelerating effect of iodine in a number of decompositions of simple organic molecules is due to a cycle of reactions involving destruction and re-formation of the iodine molecules. That work has been extended for the aldehydes so that now it is possible to give the mechanism in detail. These systems were found to be more complex than was indicated previously in that the rate of disappearance of aldehyde was definitely greater than the rate of reaction between the corresponding alkyl iodide and hydrogen iodide as calculated from Ogg's data[2] on those reactions. In fact as the temperature was lowered from the range discussed before this discrepancy increased until with acetaldehyde (to take an extreme case) the observed rate was several times as large as the one calculated on our earlier assumptions. In this paper we shall show that this discrepancy may be accounted for if we take into consideration the free radicals and iodine atoms which are present under the experimental conditions.

The reaction vessel was of Pyrex, cylindrical in shape, 15 cm. long with plane windows at both ends; the volume was approximately 250 cc. The vessel was mounted in an electric furnace that was fitted with windows so as to allow a beam of light to be directed lengthwise through the reaction vessel. The temperature was measured by a chromel–alumel thermocouple that was placed in a well extending into the reaction vessel in such a manner as not to lie in the optical path through the vessel. The furnace could be kept constant within a degree by manually regulated rheostats. The pressure was measured by a click gage, used as a null instrument, and a system that consisted of a mercury manometer and a sulfuric acid manometer connected so the mercury manometer could be used for high pressures and the sulfuric acid manometer for low pressures. The reaction vessel was connected to a vacuum line and to an iodine storage bulb, each through a heated glass valve. The iodine storage bulb was immersed in a small oil-bath that could be heated to distil iodine into the reaction vessel. The connecting tubing to the click gage and glass valves was capillary, wound with resistance wire and electrically heated to prevent the condensation of iodine. The dead space in the connections was about 2 cc.

The concentration of iodine during the course of a reaction was determined by measuring the intensity of a beam of light which passed through the reaction vessel. The light source was a thirty-two candle power automobile lamp connected through a resistance to a storage battery. A Corning glass filter No. 428 was placed between the lamp and the furnace window. The light transmitted by this filter is in the region of the maximum absorption by iodine. It has been pointed out by Cuthbertson and Kistiakowsky[3] that good results may be obtained in measuring the absorption of iodine with a blue filter while without the filter the effect of foreign gases on the absorption of iodine would cause a large error. The intensity of the beam was measured by a Weston Photronic Cell, No. 594, connected to a D'Arsonval galvanometer.

The acetaldehyde and propionaldehyde were taken from the center fractions of carefully dried Eastman Kodak Co. stock. Each sample was distilled several times and stored in three-liter bulbs connected to the vacuum line. No trouble from polymerization was experienced in storing the gases. The formaldehyde was prepared by heating trioxymethylene in a 500-cc. flask in an oil-bath. Above 200° the amount of polymer that exists in gaseous formaldehyde is very small; so no polymer could have existed in our experiments at 500°. The methyl iodide was prepared and stored similarly to the acetaldehyde. The iodine was a Merck reagent.

In order to determine the concentration of iodine present during the course of an experiment, it was necessary to make a calibration of the intensity measuring system. This was done by introducing certain amounts of iodine into the reaction vessel and by taking both the pressure reading and the galvanometer deflection. A curve could be constructed giving the relation of the light absorbed to the pressure of the iodine. To compensate for the small changes in light intensity and absorption in the reaction vessel due to tarring the galvanometer deflection with no iodine in the system was adjusted by varying the current passing through the light source.

The general procedure during a particular experiment was to introduce a certain desired amount of iodine vapor and read the pressure with the sulfuric acid manometer. The aldehyde, under higher pressure, was then introduced rapidly and an electric clock started simultaneously.

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[1] Faull and Rollefson, THIS JOURNAL, **58**, 1755 (1936).

[2] Ogg, *ibid.*, **56**, 526 (1934).

[3] Cuthbertson and Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).