[Contribution from the Chemical Laboratory of Bryn Mawr College]

The Dioxanates of the Mercuric Halides

By J. L. Crenshaw, Arthur C. Cope, Norma Finkelstein and Ruth Rogan

The cyclic diether of ethylene glycol, 1,4-dioxane, forms addition compounds with certain types of inorganic and organic compounds. The properties of these compounds are those to be expected of rather unstable oxonium salts. Several of them lose dioxane on exposure to the air, or on heating, and some apparently are dissociated into their components in solution. However, the addition compound of dioxane with mercuric chloride, according to both Paternò and Spallino[1] and Clarke[2] is stable, and sublimes unchanged on heating. Rheinboldt and his coworkers,[3] who have prepared a large number of dioxanates of inorganic halides, state[4] that the compound with mercuric chloride decomposes at 160–165°, and that with mercuric iodide at about 90°. Curran and Wenzke[5] are of the opinion that the mercuric halides do not form coördination compounds with dioxane, their evidence being the fact that diphenyl mercury has the same dipole moment in benzene and in dioxane solution. This conclusion is questionable, in view of the fact that the magnesium halides and organomagnesium halides form dioxanates much more readily than do the dialkyl (or diaryl) magnesium compounds.[6]

We have studied the properties of the dioxanates of the mercuric halides, in an effort to explain these contradictory statements. Mercuric chloride, bromide and iodide are moderately soluble in hot dioxane, and the solutions deposit colorless crystals on cooling. On exposure to the air these crystals lose dioxane in each case, the pure mercuric halide remaining. The change is very evident in the case of mercuric iodide dioxanate, since the colorless addition compound changes to the yellow and red forms of mercuric iodide, and the loss of dioxane is apparent in all three cases under the microscope. Paternò and Spallino[1] and Clarke[2] apparently failed to notice the loss of dioxane from the mercuric chloride dioxanate, and their product which sublimed was undoubtedly the residual mercuric chloride. The dipole moments of the mercuric halides as determined in dioxane solution[5] are of doubtful significance, since the solutions probably contain, not the mercuric halides, but their dioxanates.[7]

The dioxanates of the mercuric halides have been analyzed, and their dissociation pressures determined as a measure of their stability. The vapor pressures of their saturated solutions in dioxane and the vapor pressure of pure dioxane have also been measured.

Experimental Part

Materials.—Dioxane (Carbide and Carbon Chemicals Corporation) was purified by the method described by Scatchard and Benedict[8] and refluxed over sodium for two days. After fractional distillation, followed by fractional freezing, the final product had a freezing point of 11.79°, and a boiling point (760 mm.) of 101.26°, as measured with carefully calibrated thermometers. Moisture was excluded at all times, and in the determination of the boiling point a special apparatus was used.[9] These values agree well with those already reported.[8,10]

Mercuric chloride and iodide (c. p. analyzed) were used without further purification. Since the so-called c. p. mercuric bromide which was available contained about 0.5% chloride (Cl), this salt was prepared as follows. C. p. bromine was digested with a saturated aqueous solution of sodium bromide and distilled. This bromine was converted into hydrobromic acid by treatment with red phosphorus and water. C. p. mercuric oxide was dissolved in the hydrobromic acid and the resulting bromide recrystallized several times from hot water.

Vapor Pressure Measurements.—Vapor pressure measurements were made in the apparatus shown in Fig. 1, which was connected in the usual way to a vacuum pump and manometer.[11] The apparatus was cut apart at E, and 1 or 2 g. of the mercuric salt introduced into F. After resealing a current of dry air was passed through the apparatus and the whole was warmed until the salt began to sublime. The sublimed portion was then driven along by gentle heating and out of the end B. Purified dioxane was introduced into C, along with small pieces of sodium, the apparatus was tilted to the right and the dioxane refluxed for four hours, the tube G serving as an air con-

---

[1] Paternò and Spallino, *Gazz. chim. ital.*, **37**, I, 106 (1907); *Atti accad. Lincei*, **16**, V, 187 (1907).

[2] Clarke, *J. Chem. Soc.*, **101**, 1803 (1912).

[3] Rheinboldt, *et al.*, *J. prakt. Chem.*, **129**, 278 (1931); **148**, 81 (1937).

[4] Rheinboldt, *et al.*, *ibid.*, **149**, 30 (1937).

[5] Curran and Wenzke, This Journal, **57**, 2162 (1935).

[6] Schlenk and Schlenk, *Ber.*, **62**, 920 (1929); Schlenk, *ibid.*, **64**, 735 (1931).

[7] Williams, This Journal, **52**, 1838 (1930), has pointed out that the use of dioxane as a solvent in dipole moment studies is limited to compounds which do not form addition products with dioxane.

[8] Scatchard and Benedict, *ibid.*, **58**, 837 (1936).

[9] Brunel, Crenshaw and Tobin, *ibid.*, **43**, 561 (1921).

[10] Kraus and Vingee, *ibid.*, **56**, 511 (1934), give the freezing point as 11.78° and the boiling point as 101.24° (761 mm.).

[11] The arrangement was much the same as that described by Smith and Menzies, *ibid.*, **32**, 1412 (1910).

denser. The apparatus was then turned back to the position shown and dioxane distilled into D, where it was fractionally frozen three or four times, the unfrozen portions being poured back into C. C and D were cooled with solid carbon dioxide in acetone and the tube sealed off at H. Sufficient dioxane was then distilled into F and after cooling again the apparatus was sealed off at E. Cooling with solid carbon dioxide is of course necessary to prevent ignition or decomposition of dioxane vapor by the hot glass. Mercury was introduced through A into J to serve as a confining liquid. During all these operations the greatest care was taken to prevent the introduction of moisture, and the open ends of the apparatus were always protected by phosphorus pentoxide tubes. The filled apparatus was connected at A by means of heavy rubber tubing to the manometer and pump.[11] The lower part, up to I, was placed in a well-stirred bath of water or oil which was electrically heated, and provided with windows through which the mercury in J could be observed. The traps in the bulbs F, I and K form a necessary part of the apparatus. The trap in F prevented any of the mercuric halide from being carried over and fouling the mercury in J; that in I prevented any loss of mercury; and that in K kept any condensed dioxane from running back on the mercury.

The amounts of halide and dioxane introduced into F were so chosen that all the halide could be brought into solution by warming with a free flame, and on cooling no crystals would appear above the transition point. It was thus possible, in measuring the vapor pressure of the saturated solutions of the dioxanates, to be sure that no undioxanated salt was present. To ensure saturation at all temperatures the bath was adjusted to the highest temperature to be used. The solution in F was boiled vigorously under reduced pressure until a reproducible vapor pressure was obtained. Readings at lower temperatures were then taken.

The dissociation pressures of the dioxanates were measured after all the liquid in F had been boiled away and partial decomposition of the crystals had taken place. The vapor pressure of pure dioxane was also measured in the same apparatus. It was introduced in the manner already described.

Temperatures were read to one hundredth (0.01°) of a degree on calibrated thermometers. In some cases there were considerable stem corrections and though these were checked by using thermometers with overlapping ranges we do not believe the readings are accurate to much better than ±0.05°.

Pressures were read to one-tenth of a millimeter (0.1 mm.) by means of a cathetometer. A calibrated glass scale and mercury manometer were used. All pressures are given in millimeters of mercury, corrected to 0°, 45° latitude and sea level.

Table I contains the vapor pressures of each system studied, calculated for round temperatures by means of the least square equations, which are also given. The number of observations used in calculating each equation is given as well as the probable error. The equations should not, of course, be used outside of the range indicated in each case. In calculating absolute temperatures, 273.2 was added to the centigrade readings.[12]

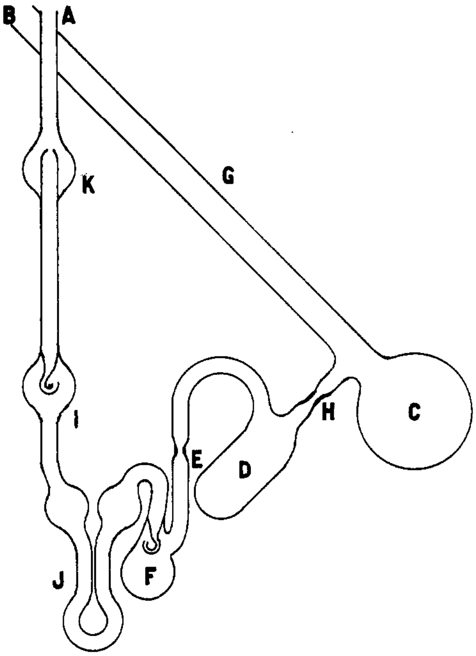

Fig. 1.

The experimental data are plotted in Fig. 2. The curves are graphs of the equations given, and are numbered to correspond with the numbers of the equations in Table I. The curves for the saturated solutions of the chloride and iodide have been omitted since they almost coincide with that for the bromide.

Discussion of Results

The vapor pressure of dioxane has been measured by several investigators. The most recent work is that of Hovorka, Schaeffer and Dreisbach,[13] whose data cover the range from 10 to 80°. Since dioxane is very hygroscopic we thought it advisable to determine its vapor pressure in our apparatus from which we think we have been able to exclude water vapor very effectively. We have extended the measurements above the boiling point and so are able to check our vapor pressure equation by means of boiling point determinations. Several determinations made at different barometric pressures in an apparatus from which moisture was excluded gave the same value for the normal boiling point (760 mm.), 101.26 ± 0.01°. This value also was obtained when metallic sodium was present in the dioxane so that we believe it is safe to assume that water was absent. The equation for pure dioxane (number 1, Table I) gives a calcu-

---

[12] Birge, *Rev. Modern Phys.*, **1**, 1 (1929).

[13] Hovorka, Schaeffer and Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

TABLE I

EQUATIONS AND VAPOR PRESSURES (MM.) AT ROUND TEMPERATURES

No. of obsns.	20	25	30	40	50	60	70	80	90	100	105	Prob. error in % P
	Dioxane–pure liquid:				(1)	$\log P = -2316.26/T - 2.77251 \log T + 16.2007$						0.37
21	28.9	37.4	47.9	76.8	119.3	179.9	264.2	378.8	531.2	730.3	850.2	
	Satd. soln. of $HgCl_2$ dioxanate:				(2)	$\log P = -1748.04/T + 1.39892 \log T + 3.96062$						1.00
12	28.2	36.3	46.5	74.3	115.5	175.2						
	Solid $HgCl_2$ dioxanate				(3)	$\log P = -2676.42/T + 0.737604 \log T + 8.36180$						0.92
12	11.3	16.3	23.2	45.4	85.5	154.9	(Trans. point solid, 67.3°)					
	Satd. soln. of $HgBr_2$ dioxanate[a]:				(4)	$\log P = -2384.81/T - 3.62617 \log T + 18.5391$						1.11
17	28.8	37.0	47.3	74.9	115.0	171.4	248.9	352.8	489.2	664.7	769.4	
	Solid $HgBr_2$ dioxanate				(5)	$\log P = -3158.99/T + 2.96571 \log T + 2.80748$						1.60
23	0.2	0.4	0.6	1.3	3.0	6.4	13.3	26.3	50.4	93.4	125.8	
	Satd. soln. HgI_2 dioxanate:				(6)	$\log P = -2263.96/T - 2.78651 \log T + 16.0546$						0.55
18	28.9	36.9	47.0	74.4	114.1	170.0	247.0	350.5				
	Solid HgI_2 dioxanate				(7)	$\log P = -3023.86/T + 11.0344$						1.25
23	5.3	7.8	11.5	24.0	47.7	91.0	167.3	297.2	(Trans. point solid, 173.1°)			

[a] Additional values for $HgBr_2$ dioxanate were obtained as follows:

Temperature, °C.	110	120	130	
Satd. soln., mm.	886.6	. . .	. . .	
Solid, mm.	168.1	294.0	491.1	(Trans. point solid, 87.7°)

lated boiling point of 101.30° at 760 mm. Considering the probable error of our equation, the agreement is as good as could be expected. Boiling points at various barometric pressures and our equation both give 23.3 mm./degree for the slope of the vapor pressure–temperature curve at the normal boiling point. If the boiling points are taken as correct the values for the vapor pressure calculated from the equation are about 0.9 mm. low in the neighborhood of the boiling point. Our calculated vapor pressures are higher at low temperatures and lower at high temperatures than those previously reported.[13]

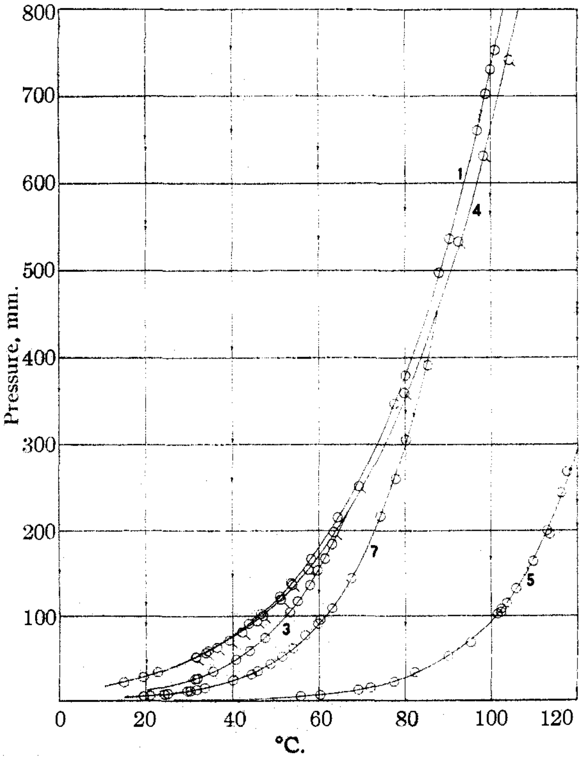

Fig. 2.—1, Dioxane; 3, $HgCl_2$·dioxanate; 4, saturated solution·$HgBr_2$ dioxanate; 5, $HgBr_2$·dioxanate; 7, HgI_2·dioxanate.

As may be seen from Fig. 2, the dioxanates of mercuric chloride and iodide have transition points which easily can be determined experimentally. The equations for the vapor pressures of the saturated solutions are for those in which the dioxanates are the solid phase. The temperatures at which the vapor pressures of these saturated solutions are equal to the dissociation pressures of the dioxanates are shown in Fig. 2. More exact values were obtained by a simultaneous solution of the equations for the saturated solution and the dissociation pressure. These calculations give 67.3° for the transition point of mercuric chloride dioxanate, and 87.7° for that of the iodide. The point for the iodide was checked by slowly heating a sealed tube containing an excess of dioxanate crystals in their saturated solution in dioxane, and observing the temperature at which the red color of mercuric iodide appeared. The point so obtained agreed with that given above to a few tenths of a degree. This method was not satisfactory for the dioxanates of the chloride and bromide as no color change occurred. The transition points of the chloride and iodide were checked also by observing the temperature at which an absorption of heat occurred when the crystals were slowly heated. The results were not very accurate since the heat absorption took place over an interval of a degree or two. This may have been due to the difficulty of stirring the crystals adequately. The transition points already given were within the range of heat absorption, provided moisture was excluded.

The behavior of mercuric bromide dioxanate seems rather surprising. As is shown in Fig. 2, its dissociation pressure, instead of being intermediate between that of the chloride and the iodide, is much lower than that of either. Under our experimental conditions it was not possible to determine the transition point of this salt. A rough estimate may be made by a simultaneous solution of the fourth and fifth equations in Table I. This gives a transition temperature of 173° at a pressure of about five atmospheres. Independent evidence of the relatively great stability of mercuric bromide dioxanate was obtained by comparing the rates at which the dioxanates of the three halides lost dioxane at room temperatures. The samples were put into open weighing bottles which were laid on their sides and protected from drafts. After four hours the losses in percentage of dioxane present were: mercuric chloride, 44%; mercuric bromide, 0.78%; mercuric iodide, 52%. This obviously crude method does not give a correct indication of the relative stability of the chloride and iodide, but it does show that the bromide is much the most stable of the three.

Rheinboldt[4] has analyzed the dioxanates of many salts and gives values which indicate that the mercuric halides combine with dioxane in the molecular ratio of 1 to 1. Since it is difficult to obtain these crystals in a pure state by the method he used, we have repeated the analyses. Crystals of the dioxanates were brought to constant weight in a stream of dry air which contained dioxane vapor at a partial pressure greater than the decomposition pressure but less than the vapor pressure of the saturated solution. The dioxane of crystallization was then removed by a current of pure dry air and the loss in weight determined. The results obtained together with those calculated on the assumption that one molecule of halide combines with one of dioxane are given in Table II.

TABLE II

COMPOSITION OF THE DIOXANATES

Dioxanate	Dioxane Obsd.	Dioxane Calcd.
$HgCl_2 \cdot C_4H_8O_2$	24.46	24.49
$HgBr_2 \cdot C_4H_8O_2$	19.65	19.63
$HgI_2 \cdot C_4H_8O_2$	16.26	16.23

From the vapor pressure measurements, the free energies of formation of the dioxanates from the solid salts and liquid dioxane (ΔF°_{298}) and the heats of formation ($-\Delta H_{298}$) have been calculated for 25° and are given in Table III.

TABLE III

FREE ENERGIES AND HEATS OF FORMATION AT 25° (CALORIES)

Compound	ΔF°_{298}	$-\Delta H_{298}$
$HgCl_2 \cdot C_4H_8O_2$	−490	3725
$HgBr_2 \cdot C_4H_8O_2$	−2750	7253
$HgI_2 \cdot C_4H_8O_2$	−925	4880

From equation 1, Table I, the molal heat of vaporization of pure dioxane is calculated to be 8960 cal. at 25°. The heat of vaporization for temperatures between 10 and 110° is given by the equation $\Delta H = 10,600 - 5.51T$.

Surface tension measurements[13] indicate that dioxane is a non-associated liquid and it should therefore give a normal value for the entropy of vaporization. At the boiling point we obtain 22.8 cal. per degree, which is somewhat larger than the value to be expected from Trouton's rule. Hildebrand's[14] modification of the rule gives 27.7 cal. per degree at 45.8°, at which temperature the molar concentration of the vapor is 0.005. This is very close to the value to be expected for normal liquids and is evidence that our values for ΔH are not greatly in error.

Summary

1. The vapor pressures of pure dioxane and of saturated solutions of dioxanates of the mercuric halides in dioxane have been measured.

2. The dissociation pressures of the dioxanates of the mercuric halides have been measured and their transition points determined.

3. Free energies and heats of formation of the dioxanates from the solid salts and liquid dioxane have been calculated.

4. The dioxanate of mercuric bromide has been found to be much more stable than the dioxanates of mercuric chloride and iodide.

BRYN MAWR, PENNA. RECEIVED JUNE 6, 1938

---

[14] Hildebrand, THIS JOURNAL, **37**, 970 (1915).