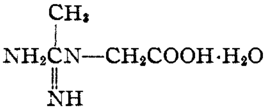
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

Dissociation Pressures of Some Organic Hydrates

BY MARY CONSTANCE LOEFFLER[1] AND WALTER J. MOORE

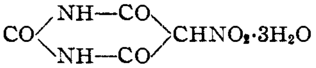
Although the dissociation pressures of inorganic hydrates have been extensively investigated, few data on organic hydrate systems appear to be available. In view of the interest in the interaction of water with organic high polymers, an investigation of the dissociation pressures of several crystalline organic hydrates was considered to be of interest. The compounds chosen for this study were:



$NH_2C(CH_3)N{-}CH_2COOH \cdot H_2O$, with CH_3 above C and $=NH$ below C

creatine hydrate

$CH_2OH(CHOH)_4CHO \cdot H_2O$ *d*-galactose monohydrate



diliturtic acid trihydrate

In addition a hitherto unreported monohydrate of dilituric acid was discovered in this investigation and its dissociation pressures were also measured.

Experimental

The apparatus used for the measurement of dissociation pressures employed a Smith–Menzies[2] isoteniscope. The hydrate sample was introduced into the isoteniscope bulb, with mercury (freshly distilled *in vacuo*) as the confining liquid in the differential manometer. After evacuation with a high vacuum system, the bulb was sealed off and the isoteniscope immersed in a liquid thermostat controlled to ±0.03°. With the aid of an observation telescope with cross-hairs the differential manometer was balanced against an external oil manometer. Pressure readings were taken at intervals of about 5° from around 30° to around 50 to 70°, the upper limit depending on the compound studied. The time required for the hydrate system to attain equilibrium varied with the substance used. Several hours sufficed for the dilituric acid trihydrate and monohydrate and for creatine hydrate. The galactose system required twenty-four to forty-eight hours. The course of the dissociation appeared to be completely reversible and the pressure–temperature curve followed in a heating cycle could be retraced on cooling.

The sources of the compounds used were the following: creatine hydrate, Eastman Kodak Co. and Paragon Testing Laboratories; dilituric acid, Eastman; *d*-galactose monohydrate, Pfanstiehl. Some of the samples were recrystallized from water, but this had no significant effect on the observed pressures.

The monohydrate of dilituric acid was prepared by desiccation of trihydrate over 70% aqueous sulfuric acid. The loss in weight at equilibrium corresponded to two moles of water per mole of trihydrate. Kjeldahl nitrogen determinations yielded 21.7 and 22.1%, the theoretical value for monohydrate being 22.0%. The trihydrate yielded 18.6 and 18.7% (theoretical 18.5%) by the same method.

Results

The observed dissociation pressures were plotted according to the Clapeyron–Clausius equation as log P *vs.* $1/T$. Excellent linear graphs were obtained from which the average heats of vaporization could be calculated.

The pressures may be expressed in the form of the equation

$$\log_{10} P \text{ (mm. of Hg)} = A - (B/T)$$

The average values of the constants determined by application of the method of least squares to the data of each run are summarized in Table I. With the tabulated constants the experimental data are reproduced to within ±2% mean deviation. Included also are the values of ΔF^0_{298}, and those of ΔS^0_{298} and ΔH^0_{298} calculated on the assumption that the dissociation heat is constant over the temperature range and that the water vapor behaves as an ideal gas.

TABLE I

System	Temperature range °C	A	B	Per mole of water vapor ΔH^0_{298} kcal.	ΔF^0_{298} kcal.	ΔS^0_{298} cal./deg.
Dilituric acid						
($3 \rightleftarrows 1$) H_2O	30–50	10.40	2880	13.20	2.91	34.5
($1 \rightleftarrows 0$) H_2O	40–70	5.74	1750	8.05	4.09	13.3
Creatine						
($1 \rightleftarrows 0$) H_2O	30–60	8.31	2200	10.05	2.67	24.8
Galactose						
($1 \rightleftarrows 0$) H_2O	40–60	7.04	1780	8.13	2.49	19.0

It is of interest to compare the values of $\Delta H°$ and $\Delta S°$ with those for the sublimation of ice, $\Delta H^0_{298} = 12.0$ kcal., and $\Delta S° = 34.6$ e. u. In contrast with inorganic hydrates for which values of $\Delta H°$ typically ranged from 12 to 18 kcal. mole, the $\Delta H°$ values for the three monohydrates investigated lie well below 12 kcal. This may be taken to be a reflection of the effect of the hydrogen bonds in the organic hydrates in increasing the crystal energy of the hydrated crystal, as compared with that of the anhydrous crystal. The low ΔS^0_{298} value for dilituric acid monohydrate is also exceptional, although the data of Christensen and Gilbert[3] yield a value of $\Delta S^0_{298} = 7.45$ for the monohydrate of hydrazine sulfate. Such low values for the entropy of hydration suggest that the water may possibly enter the crystal in somewhat random fashion, similar to the arrangements possible in zeolitic hydrates. The crystal structures of these organic hydrates, however, are not known.

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(2) A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

(3) B. E. Christensen and E. C. Gilbert, THIS JOURNAL, **56**, 1897 (1934).

Summary

The dissociation pressures of the following systems have been measured over a range of temperatures: dilituric acid (3 ⇄ 1 H_2O) and (1 ⇄ 0 H_2O), *d*-galactose (1 ⇄ 0 H_2O), creatine (1 ⇄ 0 H_2O). For the organic monohydrates both the $\Delta H°$ and the $\Delta S°$ of dissociation appear to be unusually low as compared with typical values for inorganic systems.

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The Reaction between Atomic Hydrogen and Molecular Oxygen at Low Pressures. Surface Effects[1]

BY ELMER J. BADIN

When atomic hydrogen produced by electrical discharge and molecular oxygen are allowed to react, hydrogen peroxide and water are formed. Bonhoeffer and Boehm[2] first observed that, at liquid air temperatures, large quantities of hydrogen peroxide resulted. Subsequently Geib and Harteck[3,4] showed that peroxide formation under these conditions must form by a wall reaction since it is eliminated at temperatures above −79°.

In this paper additional data of a somewhat more quantitative nature are presented for the low temperature reaction. Particular attention has been paid to water formation in order to arrive at a more satisfactory mechanism for its formation than previously proposed.

In addition, the question of whether the decrease of condensable products (peroxide and water) with increase of temperature is due solely to hydrogen atom recombination or recombination of hydroxyl or HO_2 has been considered. The study of the reaction has, therefore, been extended to a higher temperature than heretofore and the effect of surface treatment (phosphoric acid, Pyrex and potassium chloride) determined in this higher temperature region. It was expected that the effects of a potassium chloride surface (shown[5] to cause OH recombination and not H recombination) and the other surfaces would supply additional information in regard to the recombination reactions occurring.

Experimental

The trap arrangement and metering system are shown in Fig. 1. A discharge tube, G, of total length about 2.5 meters, with hollow cylindrical aluminum electrodes, F and F′, was used for dissociating the hydrogen. The tube was coated with phosphoric acid. A 15-kilovolt transformer with 110 volts a.c. primary supplied the dissociating potential. The hydrogen atom concentration, assuming all hydrogen in the products as originally in the atomic form and based on products formed in the low-temperature experiments, was estimated to be of the order of 70%.

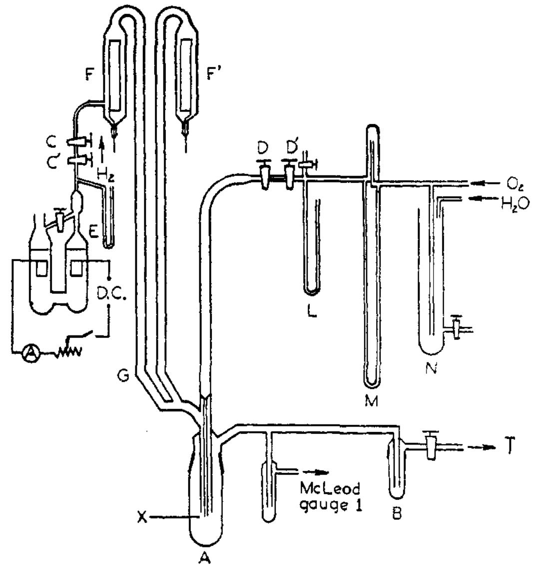

Fig. 1.—Apparatus: T, trap, McLeod gage 2, Langmuir pump, Megavac pump.

Hydrogen was introduced without drying from an electrolysis U-tube E containing dilute sulfuric acid. The gas was admitted through stopcocks C and C′ leading into one end of the discharge tube. The amount of hydrogen was determined by the quantity of electricity used. Oxygen was admitted through throttling stopcocks D and D′ from a capillary-type flowmeter M in series with a static manometer L. The oxygen flowmeter was carefully calibrated in the desired range and the flow maintained constant by an adjustable water column N. For experiments with hydrogen and oxygen both admitted to the discharge tube, a double electrolyzer was used and the premixed gases admitted. Pressures were read on McLeod gage 1 adjacent to the reaction trap A. Pressures recorded were without the discharge operating. Since pressures were measured on the exit side of the reaction trap, pressures in the discharge tube were somewhat higher.

The concentric reaction tubes X leading into trap A (51 mm. O.D.) were of 17.5 mm. and 8.0 mm. O.D., respectively. Trap B was connected to trap A by 17.5 mm. O.D. untreated Pyrex tubing. Two positions for trap B were used; the first about 100 cm. from the point of mix-

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[3] K. H. Geib and P. Harteck, *Ber.*, **65**, 1551 (1932).

[4] K. H. Geib and P. Harteck, *Z. physik. Chem.*, **170**, 1 (1934).

[5] H. S. Taylor and G. I. Lavin, THIS JOURNAL, **52**, 1910 (1930); see also A. A. Frost and O. Oldenberg, *J. Chem. Phys.*, **4**, 642 (1936); W. V. Smith, *ibid.*, **11**, 110 (1943).