[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Warming Curves for the Condensed Product of Dissociated Water Vapor and for Hydrogen Peroxide Glass

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RECEIVED FEBRUARY 27, 1956

Water vapor dissociated in an electric discharge and condensed at −196° forms a glassy product which yields O_2 gas and H_2O_2 solution when warmed. Warming curves for the discharge product are significantly different from those exhibited by H_2O_2 solution after it has been frozen rapidly to form a glass. The discharge product partially crystallizes between −110 and −75°, and the resulting crystalline phase begins to melt at about −70°. When warmed to −60° the liquid bubbles violently, evolving O_2, and the temperature suddenly rises as much as 120°. The resulting H_2O_2 solution when cooled rapidly to −196° forms a glass which crystallizes starting at about −110° with an abrupt rise in temperature to −56°, a eutectic for the H_2O_2–H_2O system. This difference in thermal behavior is interpreted as further evidence for the existence at low temperatures of an unidentified species such as H_2O–O, H_2O_3 or H_2O_4. The O_2 evolution reaction is exothermal by about 44 kcal./mole.

Introduction

The product obtained when water vapor is dissociated by an electric discharge and then condensed at low temperature and the similar product obtained by the reaction of atomic hydrogen with molecular oxygen has been studied by a number of investigators.[1–6]

The product condensed at −196° is a yellow transparent solid. On warming, the paramagnetic resonance and the yellow color disappear at about −135°.[1] Previous investigators observed that at about −115 to −110° a small amount of oxygen is evolved and the material appears to crystallize to a white solid. Further oxygen is evolved at high temperatures. In order to account for the oxygen evolution Geib and Harteck[2] have proposed the isomer of hydrogen peroxide, H_2O–O, as a product in the reaction between H and O_2 at a cold surface. Smith has suggested that the active product may be H_2O_4,[7] or complexes such as $H_2O_2 \cdot O_2$.[8] Giguère and Harvey,[5,7] on the other hand, observed that the infrared absorption spectrum of the glassy product was identical with that obtained from mixtures of H_2O_2 and H_2O and concluded that anything else must be present in very low concentration or must be infrared inactive. Both H_2O–O and H_2O_4 would be expected to have characteristic infrared absorption. Bawn and Hogg[9] observed only a small heat change accompanying O_2 evolution and attributed it to a phase change in the H_2O_2–H_2O mixture. McKinley and Garvin[6] found that more ceric ion was reduced when ceric sulfate solution was added to the cold discharge product than when the oxidant was added to the final product at room temperature.

In the paramagnetic resonance studies[1] the product of dissociated water vapor was condensed on the outside of a capillary tube of about 1 mm. diameter such that the over-all diameter of the product on the tube was only about 2 mm. When this tube was removed from liquid nitrogen and held in air at room temperature, the yellow color disappeared in a short time, then the material bubbled slightly and became sufficiently fluid to flow to the tip of the capillary. A few seconds later the drop of liquid bubbled violently for less than a second after which no further change was observed. The resulting solution contained about 50% H_2O_2. This behavior indicated that the product which normally crystallized at about −110° did not crystallize when warmed rapidly, and suggested a study of its thermal behavior. Moreover, since H_2O_2 solution was the final product, a comparison of the thermal behavior of the discharge product with that of H_2O_2 solution seemed desirable.

Experimental

Water vapor was passed at a rate of 7.7 mg./min. through a Wood's type electric discharge tube 11 mm. inside diameter and 1 meter in length. A 60 cycle a.c. potential of 2300 v. gave a current of 67 ma. under the conditions of the experiments (pressure not measured). Product was collected on a liquid nitrogen-cooled thin-walled capillary cold finger 2.5 mm. diameter located about 5 cm. from the discharge tube. After collection of sufficient product (usually 30 minutes collection time), the tube surrounding the capillary was cooled with liquid nitrogen and air was admitted to the system. The capillary with its larger connecting tube was then transferred to a vessel of liquid nitrogen wherein a 3 to 5 cm. length of the capillary was broken away from the larger tube and was transferred to an unsilvered Dewar vessel having a thin-walled inner tube 5 mm. diameter. A thermocouple junction (No. 40 copper, No. 30 constantan) was inserted into the capillary tube and connected with a 10 mv. recorder for temperature measurements. Curves reproduced in the figures were traced directly from recorder charts and therefore have non-linear temperature scales. Warming curves were started by pouring the liquid nitrogen out of the Dewar vessel and were terminated by pouring liquid nitrogen in again.

Hydrogen peroxide in the final product was determined by means of its oxidation of iodide ion.[10]

Results and Discussion

Figure 1 shows a typical series of warming curves for a single preparation of the discharge product. The characteristic yellow color of the glassy deposit disappeared simultaneously with the increased rate of temperature rise between −160 and −130°. A comparison of curve 1 with the warming curve obtained under the same conditions with no sample

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[1] R. Livingston, J. Ghormley and H. Zeldes, *J. Chem. Phys.*, **24**, 483 (1956).

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

[3] R. A. Jones and C. A. Winkler, *Can. J. Chem.*, **29**, 1010 (1951).

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[5] P. A. Giguère and K. B. Harvey, *J. Chem. Phys.*, **24**, 373 (1956).

[6] For other references to previous work see, for example, J. D. McKinley, Jr., and David Garvin, THIS JOURNAL, **77**, 5802 (1955).

[7] Paper presented at Symposium on Free Radicals: Recent Progress in Their Production, Isolation and Identification; Laval University, September, 1956.

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indicates that the apparent heat capacity of the sample was zero between −160 and −130°. It may be assumed that heat was evolved as a result of reaction between the free radicals which have been shown to disappear in this temperature range.[1] If the heat capacity is assumed to be the same as that of ice in this temperature range then the evolved heat is 8 cal./g. The paramagnetic resonance measurements[1] indicated a ratio of 1 unpaired electron present initially to roughly 150 molecules H_2O_2 in the final product. The estimate of 8 cal./g. for the evolved heat is equivalent to 3 e.v. per unpaired electron. One e.v. per unpaired electron would be expected from the reaction between OH radicals to form H_2O_2 or from the reaction between HO_2 free radicals to form H_2O_2 and O_2. However, the 8 cal./g. heat evolved can only be considered as an estimate of the upper limit, since amorphous ice obtained when water vapor is condensed on a surface at −196° evolves about 11 cal./g. when warmed the first time to −125°.[11] Ordinary water vapor or a mixture of water and hydrogen peroxide vapor yields an opaque white solid when condensed at −196°, but dissociated water vapor condensed under the same conditions yields a transparent solid. This difference suggests the possibility that dissociated water vapor condenses initially to give a liquid or solid in which the molecules have sufficient mobility to exclude voids from the condensate, while water or hydrogen peroxide molecules remain immobile at −196° after condensation.

Curve 1 of Fig. 1 was terminated at −120° by pouring liquid nitrogen into the Dewar vessel and curve 2 was started about 30 seconds later after the liquid nitrogen had been poured out again. The warming rate changed only very slowly up to about −129° where it decreased by a factor of about 2. This reproducible decrease in warming rate is attributed to a glass transition.

At about −110° the material began to foam gently and became white and opaque, presumably as a result of small gas bubbles in the viscous liquid. The increase in warming rate when foaming began could be due to a small amount of heat evolved from a chemical reaction, or to heat of crystallization. Although crystallization at about −110° has been observed under a variety of conditions by previous investigators, it was not possible in this experiment to determine by visual inspection whether crystallization was occurring in the foam. The warming rate decreased markedly above −65° (Fig. 1, curve 2) indicating absorption of heat by the sample. At −60° the sample began to bubble violently and the temperature rose from −58 to +63° in less than 4 seconds (faster than could be followed by the recorder).

The resulting hydrogen peroxide solution, after it had cooled to room temperature, was transferred from the outside of the capillary tube on which the product had been collected to the inside in order to duplicate more nearly the original vertical distribution of sample in the Dewar vessel (and also to avoid breaking the vessel when the sample was cooled). When liquid nitrogen was poured into the Dewar vessel the solution froze to a clear glass. Glasses prepared from D_2O_2 have been observed previously by Giguère and Secco,[12] but no thermal analysis was made.

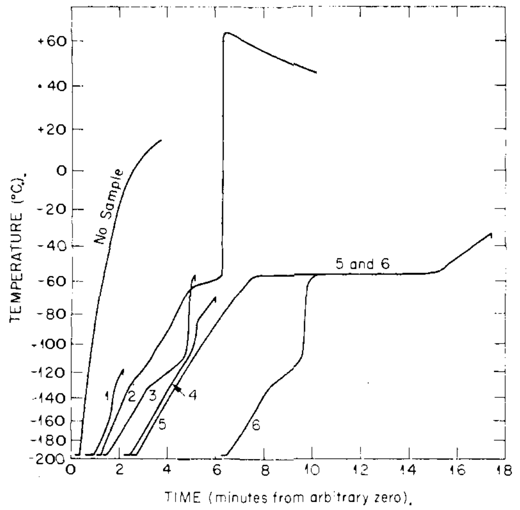

Fig. 1.—Successively recorded warming curves for one preparation of condensed product of dissociated water vapor and for the final H_2O_2–H_2O mixture. Outer tube of Dewar vessel at 25°.

Curve 3 (Fig. 1) shows the warming behavior of the hydrogen peroxide glass. The glass transition appears at −132°, about 3° lower than the temperature of the glass transition in the original glassy deposit. Starting at −110°, the sample changed from a clear viscous liquid to opaque white in appearance and the temperature rose abruptly to −56°, a eutectic temperature[13] for the H_2O_2–H_2O system. The sample was cooled immediately and allowed to warm again. Curve 4 shows a small decrease in slope at the glass transition temperature and a rapid rise from −100 to −85° attributable to heat of crystallization, indicating that crystallization was incomplete when curve 4 was started. Curve 5, the warming curve for the crystalline solid, shows no significant change between −196° and the eutectic temperature. The solid was allowed to melt completely before the sample was cooled again. Curve 6 shows the same phenomena as curve 3 and is identical with curve 5 beyond the intersection of the two curves. The fact that less time was required for melting the crystalline phase in curve 6 than in curve 5 indicates that crystallization was not complete when the eutectic temperature was reached in curve 6. The last of the crystalline solid disappeared near the eutectic temperature indicating a composition close to that of the eutectic, 61.2 wt. % H_2O_2. Actual analysis showed 55 wt. % H_2O_2.

The series of warming curves in Fig. 2 are similar to those in Fig. 1 except that for some of the curves slower warming rates were obtained by immersing the Dewar vessel in a bath at −78°. Curve 1 of Fig. 2 shows the same behavior as curve 1 of Fig. 1. Curve 2 shows a decrease in warming rate from 9°/

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[12] P. A. Giguère and E. A. Secco, *Can. J. Chem.*, **32**, 550 (1954).

[13] W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corp., New York, N. Y., 1955, p. 211.

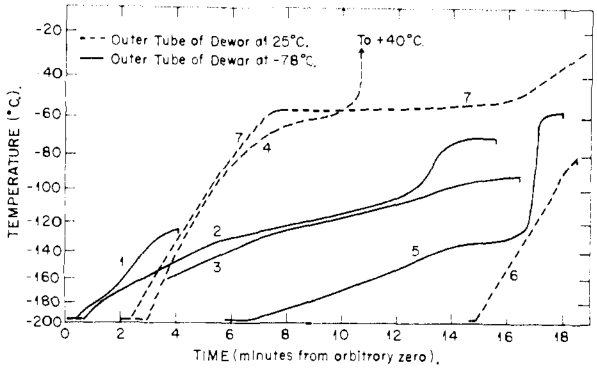

Fig. 2.—Warming curves for another sample of condensed product of dissociated water vapor and for the resulting H_2O_2-H_2O mixture with outer tube of Dewar vessel at indicated temperature during the measurements.

min. just below −133° to 4°/min. above −129°, indicating a glass transition at about −131°, a temperature about 2 degrees lower than that observed with faster warming. At about −110° the warming rate began to increase and the temperature rose from −95 to −75° in one minute; however, unlike curve 2 of Fig. 1, the temperature did not rise above −70 due to the lower temperature of the outer Dewar wall. Curve 3 shows the glass transition at −131° and shows little change in rate from −128 to −90°. The outer wall of the Dewar vessel was allowed to warm to room temperature before curve 4 was started, in order that the exothermal reaction could go to completion.

In every case, after the discharge product reached room temperature, the thermal behavior of the resulting solution was the same as that of solution prepared by dilution of 80% H_2O_2. Comparison of curves 2 and 4 (Fig. 2) for the initial product with the corresponding curves, 5 and 7, respectively, for the final hydrogen peroxide solution reveals some significant differences. The rapid rise in curve 5 due to crystallization leaves the sample very close to the eutectic temperature −56°. In curve 2, on the other hand, the rapid rise starts at a higher temperature and takes the sample only to −70°, considerably below the H_2O_2–H_2O eutectic. Curve 4 still shows the glass transition (observable in the original recording but lost in the tracing reproduced in Fig. 2) indicating incomplete crystallization. Curve 4 shows a marked decrease in slope beginning at about −85°, while curve 7 continues to the H_2O–H_2O eutectic, −56°, with little change in slope. This decrease in slope of curve 4 indicates heat absorption by some process within the sample, and the most probable process of this type is the melting of a crystalline phase.

Warming curves for other concentrations of H_2O_2 ranging from 30 to 80% showed the same rapid temperature rise accompanying crystallization. When a glass was warmed the rapid rise always started between −115 and −110° and terminated at the appropriate eutectic temperature, −52 or −56°. When partially crystallized material was warmed the completion of crystallization was indicated by an abrupt change in warming rate to that observed when the completely crystallized material was cooled and allowed to warm again (as in curve 4 of Fig. 1). When H_2O_2 solutions in the Dewar vessel were cooled slowly by immersing the vessel in liquid nitrogen the observed cooling curves indicated a much slower rate of crystallization at any specific temperature, even at temperatures as low as 10° below the eutectic. It seems reasonable that the number of crystal nuclei formed when a liquid is cooled slowly should be less than the number formed when the same liquid is cooled quickly to a glass and allowed to warm. In a series of 16 warming curves for H_2O_2 concentrations from 30 to 80% of the glass transition temperature appeared to be constant, −133 ± 1°. The 30 and 80% solutions were usually observed to be partially crystalline after the 2 mm. diameter thin-walled tube containing the solution was cooled rapidly with liquid nitrogen. A 97% H_2O_2 solution became opaque white as if completely crystallized when cooled; however, warming curves showed a rapid temperature rise from about −107 to −97° indicating additional crystallization.

The evolution of oxygen and heat from the discharge product when it is warmed above −60° might be attributable to the decomposition of H_2O_2 in a chain reaction initiated by a small amount of some unstable species. However, the warming behavior of the product below −60° is distinctly different from that of a mixture of H_2O_2 and H_2O and indicates the presence of an appreciable concentration of at least one other component. The disappearance of paramagnetic resonance absorption at −135° implies that only species having an even number of electrons exist in the system at higher temperatures. Thus to explain the observed warming behavior it seems reasonable to postulate the existence below −60° of a molecular combination of hydrogen and oxygen which is not stable above −60°.

The exact composition of the dissociated water vapor when it reaches the cold surface is not known. Foner and Hudson[7] have observed H, O, OH, HO_2, O_3, H_2, O_2, H_2O_2 and H_2O in partially dissociated H_2O_2 vapor and each of these may be present to some extent in the dissociated water vapor. However, the species which are important in the reaction which leads to the condensed product on a liquid nitrogen cooled surface may be assumed to be H, OH and O_2. Water vapor reaching the surface would merely condense without further reaction. High activation energies probably inhibit reactions of H_2 with OH or HO_2 at −196°, and this may account for the fact that H_2 is the chief product beyond the cold trap (98% H_2 in one measurement). Other possible species may be assumed to be present in negligibly low concentrations. Since H_2O_2 is not present in significant concentrations in the gas[6] it must be formed in the final product either during or following condensation.

The large quantity of product deposited near the tip of the capillary (nearest the discharge tube) indicates that the reactants are removed rapidly from the flowing gas. The only reactant which would be expected to have a low enough vapor pressure to condense normally on the cold surface is OH; however, both H and O_2 may be adsorbed on the cold surface. Geib[14] has proposed a mechanism for peroxide formation in which H atoms adsorbed on the cold surface react with O_2 molecules from the gas to form HO_2 free radicals which subsequently react with H atoms to give H_2O_2. Since OH is known to be present in significant concentrations,[15] the formation of condensed product from dissociated water vapor cannot be this simple; however, the mechanisms may involve reaction of adsorbed species with molecules from the gas. Smith[8] has proposed that the free radical complexes $HO{\cdot}O_2$ and $HO_2{\cdot}O_2$ might be fairly stable. Formation of these species provides a possible mechanism for retention of O_2, and their subsequent reaction with H atoms could result in the formation of H_2O_3 and H_2O_4. These same molecular species might also be expected as products in the low temperature reaction of HO_2 with OH or HO_2.

The amount of heat evolved can be estimated from the data shown in Fig. 1. Using the heat capacity 0.757 cal./g. given by Giguère and Morissette[16] for 60.1% H_2O_2 in the range 0 to 27° and applying a 28% correction for the heat capacity of the Dewar tube and thermocouple, one finds that the temperature rise from -58 to $+63°$ represents a heat evolution of 118 cal./g. From the ratio of evolved oxygen to final H_2O_2 (1:5.8) obtained from the data of Jones and Winkler,[3] the calculated heat evolved is 44 kcal. per mole of evolved oxygen. Only a small fraction of the gas appeared to be evolved below $-60°$. Within wide limits of possible error, this agrees with the amount of heat expected from the decomposition of H_2O_2 (48 kcal. per mole of evolved oxygen), and it also agrees with the amount to be expected from the decomposition of H_2O_3 or H_2O_4 if the reactions $H_2O_3 \rightarrow OH + HO_2$ and $H_2O_4 \rightarrow 2HO_2$ are assumed to be only slightly endothermal. The decomposition of $H_2O{-}O$ to form O_2 would yield only slightly less than the heat of dissociation of O_2, 116 kcal./mole, if the heat absorbed in the reaction $H_2O{-}O \rightarrow H_2O + O$ is small. Thus the observed heat associated with O_2 formation seems to favor intermediates such as H_2O_3 or H_2O_4.

Neither Robertson[17] nor Foner and Hudson[7] were able to detect HO_4 or H_2O_4 mass spectrometrically in a gas at room temperature containing HO_2 and O_2; however, this does not preclude the formation and existence of these species at lower temperatures. Below $-60°$, H_2O_3 and H_2O_4 would have low vapor pressures, perhaps too low to permit their detection in a mass spectrometer.

It should be pointed out that the conclusions from the data presented here do not support recent claims[18,19] for the existence of H_2O_4 at temperatures considerably above $-60°$.

Acknowledgments.—The author is grateful to Ralph Livingston and Henry Zeldes for many helpful discussions.

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OAK RIDGE, TENNESSEE

[CONTRIBUTION NO. 2128 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Distribution of Tripositive Arsenic between Hydrochloric Acid Solutions and β,β'-Dichlorodiethyl Ether

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RECEIVED OCTOBER 1, 1956

The distribution of tripositive arsenic between aqueous hydrochloric acid solutions and β,β'-dichlorodiethyl ether has been investigated. The hydrolysis products from the ether phases have been analyzed and the ratios of chloride to arsenic established at various aqueous hydrochloric acid concentrations. These ratios vary with the hydrochloric acid concentration which indicates that more than one chloride species of arsenic is present in both phases. Analysis of the distribution data and of solubility data taken from the literature has permitted the calculation of formation constants for the proposed species.

Introduction

This work was undertaken in an effort to establish some basis for predicting what compounds of tripositive arsenic exist in aqueous hydrochloric acid solutions. Preliminary work in this Laboratory[2] and that of Irvine and co-workers[3] have shown that tripositive arsenic can be extracted from hydrochloric acid solutions by a number of organic solvents. Of these, β,β'-dichlorodiethyl ether appeared to be most suited for the desired study, since it is easily purified, easily handled and dissolves only small amounts of hydrochloric acid and water while dissolving relatively large quantities of arsenic. Correlation of the results of this work with conductivity,[4] solubility[5,6] and electromotive force data[7] permits the prediction of the

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(1) Department of Chemistry, University of Missouri, Columbia, Missouri.

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