THE ABSORPTION SPECTRUM AND PHOTOCHEMICAL DECOMPOSITION OF HYDRIODIC ACID

BY G. K. ROLLEFSON AND J. E. BOOHER

The photochemical decomposition of hydriodic acid has been the subject of investigation from time to time for fifty years. The first mention of the reaction was by Lemoine[1] but the first detailed investigation was carried out by Bodenstein.[2,3,4] The quantum yield was determined by Warburg[5] for the wave lengths 2070, 2530 and 2820 Å. and found to be approximately two. This value was found to hold for wave lengths slightly greater than 3000 Å. by Bodenstein and Lieneweg. Coehn and Stuckardt[6] have investigated the reaction in quartz, uviol and Jena glass vessels using a quartz mercury arc as a source of light and found that the reaction occurred in all the vessels but was markedly slower in those of glass than in the quartz or uviol.

The absorption spectrum has been studied by several investigators,[6,7,8] who report essentially the same results, namely, a continuous absorption extending from 3340 Å. toward shorter wave lengths. Bodenstein and Lieneweg report slight absorption as far as 3600 Å.

These results have led to the decomposition being ascribed to the dissociation of an hydriodic acid molecule into a normal hydrogen atom and an iodine atom in the $^2P_1$ state followed by the reaction of the hydrogen atom with a second molecule of hydriodic acid. The iodine atoms produced combine to form molecules either by triple collision in the gas phase or at the walls. This explanation seems adequate for those wave lengths transmitted by quartz or uviol glass but in the case of decomposition in ordinary glass vessels we must assume either another mechanism, since the reported absorption is beyond the transmission limit of ordinary glass, or else the absorption must extend considerably beyond the limit given above. The observation of Salant and Sandow in their work on the Raman effect for hydriodic acid gas[9] that the 4047 Å. line of the mercury arc caused decomposition emphasizes this fact. The experiments described in this paper were designed to clarify the situation concerning this reaction in the long wave length region.

[1] Lemoine, *Ann. chim. phys.*, [5], **12**, 145 (1877).

[2] Bodenstein, *Z. physik. Chem.*, **22**, 23 (1897); [3] **85**, 329 (1913).

[4] Bodenstein and Lieneweg, *ibid.*, **119**, 123 (1926).

[5] Warburg, *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).

[6] Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

[7] Bonhoeffer and Steiner, *ibid.*, **122**, 187 (1926).

[8] Tingey and Gerke, THIS JOURNAL, **48**, 1838 (1926).

[9] Salant and Sandow, *Phys. Rev.*, **6**, 1591 (1930).

The hydriodic acid used in the experiments we have performed was prepared by dropping a concentrated solution of the gas onto phosphorus pentoxide. The gas evolved was purified by passing it through a tube filled with phosphorus pentoxide and condensed with liquid air. It was distilled from the solid state, condensed in a tube the walls of which were covered with a film of mercury and this process was repeated several times. The final product was distilled into the reaction vessels or absorption tubes as needed. A water white product was obtained.

The first tests were to determine whether the decomposition could be sensitized by iodine. For this purpose several tubes of Pyrex glass were filled with the gas to one atmosphere pressure and various amounts of iodine added. These were illuminated by a bank of tungsten filament lamps for two days at a temperature of approximately 175° and the amount of decomposition determined by absorbing the iodine and hydriodic acid and measuring the residual hydrogen. The results showed no sign of any sensitization by the iodine, which is in agreement with the observation made by Bodenstein and Lieneweg at one pressure of iodine.

Ångström units.

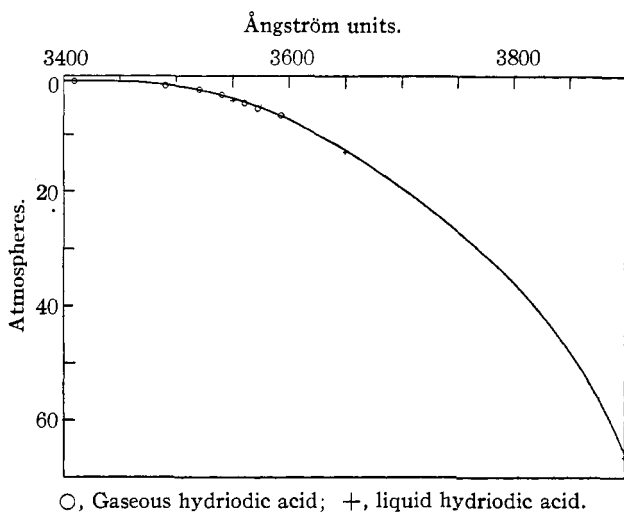O, Gaseous hydriodic acid; +, liquid hydriodic acid.

Fig. 1.

In order to determine whether any decomposition was caused by visible light, three tubes were filled with pure hydriodic acid gas. One of these tubes was left in the dark and the other two were exposed to sunlight for about two weeks. One was surrounded by water and the other by a solution of quinine sulfate, which absorbed all light of wave length less than 4050 Å. On opening the tubes it was found that there had been no reaction in the tube left in the dark or in the one surrounded by the quinine sulfate solution, but the third one showed about 25% decomposition. This indicated that the decomposition must be attributed to absorption of light of wave length less than 4050 Å.; therefore we turned our attention to an investigation of the absorption in this region.

As we were primarily interested in determining whether the absorption extended to longer wave lengths than 3300 Å., it was possible to carry out the observations using vessels of Pyrex glass. The absorption spectrum of the gas was determined using a tube 175 cm. long with an internal diameter of 1.5 cm., and the pressure of the gas was varied

from 1 to 8.5 atmospheres. The source of light was a 6-volt, 108-watt tungsten filament lamp which gives a continuous spectrum extending to approximately 2700 Å. The absorption tube, however, did not transmit wave lengths shorter than 3200 Å. The spectra were photographed with a Hilger quartz spectrograph. The absorption was perfectly continuous and at the highest pressure the edge of the blackening on the plate appeared at approximately 3550 Å. The variation in the absorption with pressure is shown in Fig. 1 by plotting the limit of the blackening on the photographic plate against the pressure. It is apparent that the absorption extends considerably beyond the limit of 3340 Å. given in the literature. Furthermore, it is obvious from the trend of the points that the limit of the absorption has not been reached even at the highest pressures used. The absorption for greater concentrations of hydriodic acid was carried out using the liquid. That such measurements could be used to extend the measurements on the gas was shown by comparing the absorption of a one-centimeter thick layer of liquid with the absorption of a layer of gas having the same value for the concentration times the thickness, i. e., a column 175 cm. long at a pressure of 4.4 atmospheres.

The absorption appeared to be identical for both conditions so the measurements were extended using the liquid up to a layer fifteen centimeters deep. The results were calculated to equivalent gas pressures in the long tube and plotted with the data on the gas in Fig. 1. The points plotted are for exposures of twenty seconds. From the curve we see that the absorption extends at least as far as 3900 Å. With shorter exposures a limit between 3950 and 4000 Å. was reached.

From the results which have just been given it is apparent that the absorption limit of 3340 Å. given in the earlier work is not a true limit characteristic of the gas. Such being the case, the interpretation of the absorption limit as corresponding to the energy of dissociation of the HI molecule into a normal hydrogen and an excited iodine atom becomes invalid. By this we do not mean that there is no absorption corresponding to such a process but rather that the observed absorption is due to a combination of this process with a dissociation into normal atoms. The value for the heat of dissociation of HI into normal atoms as calculated from thermal data is 69,000 cal. or 3 volts. The energy necessary to raise an iodine atom to the first stage of excitation is 0.95 volt. From these data it is readily calculated that the longest wave length which should dissociate the molecule into a normal hydrogen atom and an excited iodine atom is 3120 Å., whereas the value for both atoms in the normal state is 4120 Å. On this basis we should interpret the continuous absorption found between 3120 and 4000 Å. as causing a dissociation of the molecules into normal atoms, the excess energy going into kinetic energy of the atoms. The absorption at wave lengths less than 3120 Å. may be due partly to this process and partly to dissociation plus activation of the iodine, with the excess energy going into translational energy of the atoms.

The occurrence of two absorption processes of this type differing only in the excitation of the iodine atom is similar to the behavior of sodium iodide[10] except that in the latter case the intensity distribution was such that two well-defined maxima were readily distinguished. In the present case the

[10] Franck, Kuhn and Rollefson, Z. Physik, **43**, 155 (1927).

intensity distribution may be explained by assuming that the potential energy curves[11] for the normal and two excited states are as shown in Fig. 2. The curve A represents the normal state with a strong chemical binding, which is to be correlated with the relatively large value for the magnitude of the fundamental vibration quantum, ν (cm.$^{-1}$) = 2233, found by Salant and Sandow[9] in the Raman spectrum of the gas.   The upper states B and C represent much weaker bindings with the minima of the potential curves lying at a much greater separation of the nuclei than for A.   Due to the magnitude of the vibration quantum in state A the absorption will be almost entirely from the zero or first vibrational states.   On our diagram this is represented by the region between the vertical lines *ab* and *cd*. The portions of the curves B and C lying between these lines represent energies greater than the heats of dissociation of the respective states and therefore when absorption occurs we find it to the short wave length side of the minimum energy necessary for dissociation.

Fig. 2.

The dissociation products for curve B are normal atoms and for C a normal hydrogen atom and excited iodine atom.   No dissociation products have been indicated for the lowest state, A, as the available evidence does not allow a definite decision.   From the fact that HI shows an infra-red rotation and rotation–vibration spectrum in absorption, we may conclude that the binding is fairly polar in character. It is quite likely that in the zero and first vibrational levels the molecule may be considered as an example of ionic binding.

The mechanism of the photochemical decomposition is essentially the same for all effective wave lengths.   The first step is

$$HI + h\nu = H + I \text{ or } I^*$$

followed by

$$H + HI = H_2 + HI$$
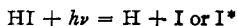
and the recombination of the iodine atoms.   Since the iodine atoms do not enter into any reaction affecting decomposition, it makes no difference whether the iodine atom formed in the initial step is activated or not.

[11] Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).
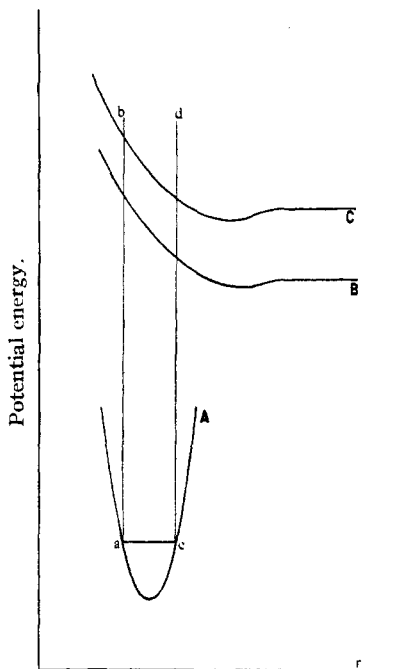
The slowness of the reaction in glass vessels is to be attributed to the small absorption coefficient for wave lengths transmitted by glass.

Summary

It has been shown that the continuous absorption of hydriodic acid extends up to a wave length of 4000 Å. instead of terminating at 3340 Å. as reported by others. The absorption on the long wave length side of 3120 Å. has been interpreted as due to the dissociation of the molecule into normal atoms and that on the shorter wave length side as due to a dissociation with the iodine atom excited. The intensity distribution of the absorption has been discussed with reference to the potential energy curves for the normal and excited states of the molecule. The photochemical decomposition of hydriodic acid has been shown to be due to this absorption and the mechanism of the reaction has been discussed.

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THE ELECTROMETRIC AND CATALYTIC DETERMINATION OF HYDROGEN-ION CONCENTRATION. THE MEAN ACTIVITY COEFFICIENTS OF THE IONS OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS[1]

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In connection with some work on the dissociation constants of indicators in aqueous salt solutions it became necessary to have buffer solutions of known hydrogen-ion concentration. Most buffer systems are standardized in terms of hydrogen-ion activity, the determination being based on certain non-thermodynamic assumptions regarding diffusion potentials. Where the classical dissociation constant is known in a given salt solution, the hydrogen-ion concentration can be calculated. However, accurate values of the dissociation constants are known for few acids except in very dilute solutions. The purpose of the present work is to determine the hydrogen-ion concentration of a series of benzoate–benzoic acid buffers in aqueous solutions of potassium chloride by two different methods. At the same time the mean activity coefficient $\sqrt{f_{H^+}\ f_{B^-}}$ will be obtained. The method of determining $f_{H^+}\ f_{B^-}$ the product of the activity coefficients, is as follows. The thermodynamic dissociation constant is equal to