interpreted in the light of physical principles which include the screening effect. By extending the Bohr concept of elliptical orbits to shared electrons it follows that a displacement of an orbit in one part of a molecule causes displacement of the other electron orbits in the same general direction. When these concepts are applied to the Pauling model of benzene, we obtain displacement formulas of benzene derivatives which indicate the relative attractive forces between the carbon nuclei and the electrons in the respective carbon-hydrogen bonds. These formulas account for the relative reactivities of substituted benzyl chlorides and bromides and for the phenomena of substitution.

A measure of the relative electron attractions of radicals is given by the ionization constants of *para* substituted benzoic acids.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 180]

THE ULTRAVIOLET ABSORPTION SPECTRA AND THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDROGEN BROMIDE AND IODIDE

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The purpose of this investigation was to study the ultraviolet absorption spectra of the hydrogen halides during photochemical decomposition in order to test the validity of two alternative mechanisms which have been suggested to explain the existing experimental facts.

Before the quantum theory of band spectra of molecules had received its great development Warburg[2] suggested the following mechanism, which was in accord with his experimental observations. The absorption of a quantum of ultraviolet light decomposed a single hydrogen halide molecule into atoms which late reacted with another hydrogen halide molecule in such a manner as to produce one hydrogen and halogen molecule. More recently Stern and Volmer,[3] in view of the recent developments on the theory of band spectra have assumed that the absorption of the radiation did not produce direct photochemical decomposition, but that it did produce an excited molecule which would, upon collision with another hydrogen halide molecule produce one hydrogen and halogen molecule. With the aid of the quantum theory of band spectra[4] it is possible to

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[1] From the Doctor's Dissertation of Harold C. Tingey, Massachusetts Institute of Technology.

[2] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1916**, 314; **1918**, 300.

[3] Stern and Volmer, *Z. wiss. Phot.*, **19**, 275 (1920).

[4] Sommerfeld, "Atomic Structure and Spectral Lines," translated from third German Edition by Henry L. Brose. E. P. Dutton and Company, New York, **1923**.

predict the type of absorption spectrum which corresponds to either of the above mechanisms. Thus, a band absorption spectrum would be expected to be found if the Stern and Volmer mechanism were correct. On the other hand, if Warburg's mechanism were true the absorption spectrum would not consist of bands, but would probably be continuous, which is analogous to atomic absorption spectra of similar origin.

The absorption spectra found for pure hydrogen bromide and hydrogen iodide in this research appear continuous. Reasons are given which support the thesis that they are truly continuous and the results are in agreement with Warburg's mechanism.

Experimental Part

Hitherto, a monochromatic light source has been the ideal in exact photochemical experimentation. On the contrary, in this research a source of light which emits a continuous spectrum was necessary to reveal the structure of the absorption spectrum. The experimental procedure consisted in photographing the ultraviolet spectrum of a source of light which emitted a continuous spectrum with and without the interposition of a quartz-absorption tube containing the pure gaseous hydrogen halide.

The Vacuum Line.—This was constructed of Pyrex glass, and was pumped by a mercury diffusion pump, backed up by an oil pump capable of producing a vacuum of 0.001 mm. The McLeod gage read down to 0.00001 mm., and with the pumps going the pressure could be reduced much further.

Sources of Ultraviolet Radiation.—For a reference standard, the cadmium spark spectrum was used. It was excited by high frequency current from a coil for this purpose discharging at about 3000 volts between cadmium electrodes.

For the production of band absorption spectra, a source of continuous ultraviolet radiation is necessary, and it is highly desirable that the intensity should be uniform throughout the range of wave lengths. Good results cannot be obtained with a metal spark spectrum on account of the lines. The source used in these experiments was a hydrogen discharge tube. It was made of 6mm. Pyrex glass tubing, with a polished quartz window 1 mm. thick cemented with de Khotinsky cement on one end. The electrodes were tungsten wire spirals. The tube was filled with dry electrolytic hydrogen at about 15 mm. pressure, the optimum operating pressure being determined by slowly reducing the pressure while the discharge was passing. The current was supplied by the high frequency coil. An intense, striated discharge resulted, blue at first, but changing to pink as the tube became hot.

The radiation from this tube was focused on the spectrograph slit, and the spectrum was continuous and uniform,[5] without lines, for wave lengths

[5] The intensity fell off in the region 2200–2000 Å.

between 4000 Å. and 2000 Å., the short-wave limit of the spectrograph used. The spectrum showed lines (unidentified) in the visible and near ultraviolet down to 4000 Å., but these did not interfere with the present experiments. The one draw back to this source was that it required exposures of about an hour, compared with one minute for the cadmium spark.

The Spectrograph.—A small Fery spectrograph, manufactured by Ch. Beaudouin, was used. A cylindro-spherical quartz lens throws an elongated image of the source on the slit. Light from the slit enters the prism, is reflected from its curved back, and is thus focused on the photographic plate. Three exposures could be made on one plate. The entire spectrum from 8000 Å. to 1800 Å. was obtained in one exposure, and covered a length of about 8 cm. The plates used were the Eastman Kodak Company Seed's L. Ortho Plates. They were developed in pyro-tank developer at 17° for 30 minutes.

The Absorption Tubes.—Two absorption tubes made entirely of transparent fused quartz were used in the experiments. Both were cylindrical, of 4 cm. diameter. Tube No. 1 was 12 cm. long, and had two side arms, distant about 3 cm. from the ends. Tube No. 2 was 23 cm. long, and had a single side arm near one end. The ends were clear and polished and were about 1 mm. thick. During most of the experiments the side arms were sealed by means of graded seals to Pyrex glass, so that the tubes could be joined directly to the rest of the apparatus without the use of cemented joints. This, together with the all-quartz construction of the tubes, made it possible to evacuate them at high temperatures, thus eliminating absorbed impurities.

Tube No. 3, used in some of the experiments, was a length of Pyrex tubing 90 cm. long and 20 mm. in diameter, with quartz end-windows 1 mm. thick cemented on with de Khotinsky cement.

Preparation and Purification of the Hydrogen Halides.—The hydrogen halides were prepared by dropping 85% orthophosphoric acid, of analytical grade of purity, on the potassium salts (prepared by five recrystallizations of the c. p. product), in the apparatus of Fig. 1. A dropping funnel A is fitted by ground-glass joint B into a 250cc. flask C, which contains the salt. D is a trap to condense water, E a phosphorus pentoxide tube containing a vertical column of this substance about 20 cm. long. The system was evacuated to 0.0001 mm., then orthophosphoric acid (previously boiled) was admitted, and the reaction was started by warming. The hydrogen halide, with some water, passed through D, where most of the water condensed; then through E, where the rest of the water was removed; and finally to the trap F, where it was condensed by liquid air. The 4-liter bulb H, evacuated to 0.0001 mm., was shut off at G during this procedure. When enough material had collected in F, the apparatus was sealed off at J, and the system thoroughly evacuated through I, keeping the hydrogen halide frozen. The stopcock I was then closed, and the gas allowed to evaporate through G into H; the last portion, which contained visible amounts of free halogen, was rejected. In this way a bulb of the hydrogen halide at atmospheric pressure, free from water, and from phosphorus and mercury compounds, was obtained. The freshly prepared material froze to a pure white solid; it melted sharply and at constant pressure; this pressure (as read on a capillary manometer) was within 2 mm. of that calculated from the equations of Henglein[6] for the vapor pressures of hydrogen bromide and iodide. Hydrogen bromide, and to a greater extent hydrogen iodide, decomposed slowly on standing in these bulbs, giving free halogen, which also attacked the stopcock grease. Impurities thus introduced were, however, removed in filling the absorption tubes as described below.

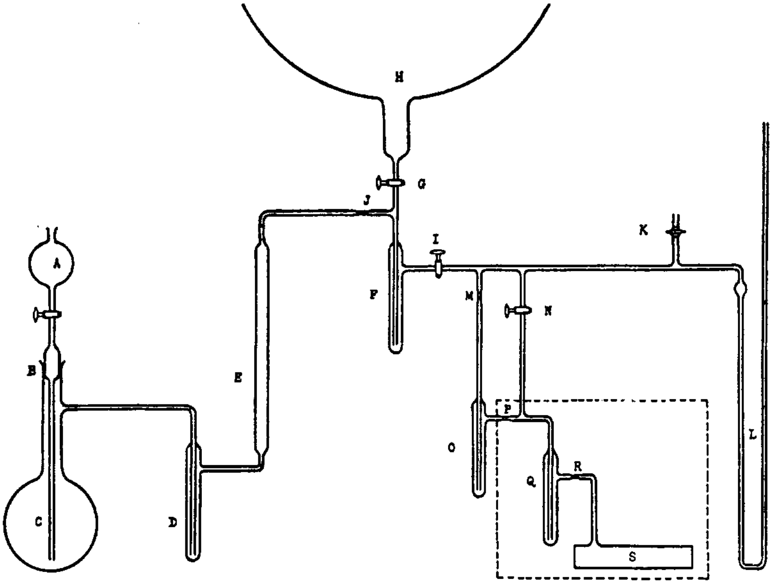

Fig. 1.

Filling the Absorption Tubes.—In the first experiments, hydrogen bromide was led directly from the generator into the absorption tube; spectrographic evidence was obtained of an impurity, and thereafter the gas was purified by distillation as follows.

Referring to Fig. 1, F-G-H-I is the storage bulb previously described; stopcock K affords connection to the vacuum line and McLeod gage; L is a mercury manometer on which pressures from 0 to 2 atm. could be read; O and Q are traps; S is the absorption tube. The portion of the

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[6] Henglein, *Z. Physik*, **18**, 64 (1923).

apparatus inclosed by the dotted lines can be surrounded by an electrically heated oven.

The system was thoroughly pumped out with the stopcock I open; then the oven was heated to 550°, and the pumping continued for an hour at this temperature. During the heating appreciable amounts of gas, consisting mainly but not entirely of water vapor, were given off. During the last half hour, the stopcock N was closed, and the trap O immersed in liquid air. The oven was removed, and the liquid air transferred to trap Q. In this way it is believed that all water and mercury vapors were removed and kept from the tube S. The trap O was sealed off at H and P before it warmed up. Now with the stopcock I closed, all the gas in H was condensed and frozen in F, and allowed to evaporate back into H until the material had melted and boiled for some time. Then G was closed; the material left in F was frozen, and allowed to sublime slowly from F to Q (which was still surrounded by liquid air), until enough had accumulated. Then with I closed the material in Q was evaporated until the desired pressure was reached, when the absorption tube was sealed off at R.

It was found that the baking out had no effect on the spectrum obtained, so this procedure was omitted in most of the experiments except those on the electrical conductivity of the gas. The redistillation, however, was carried out in all cases.

Experimental Results

Absorption of Spectra of HBr and HI.—The tables give the results of the experiments on the absorption of radiation by hydrogen bromide and iodide. The temperature was that of the room except in Expts. 9, 10 and 11 when it was 25°, 250° and 400°, respectively.

In Tables I and II, the time given is the length of exposure; the temperature and pressure are those of the absorbing gas; "Tube No." refers to the absorption tube; "Plate No." identifies the photographic plate; "L" is the length in centimeters of a column of the gas at one atmosphere pressure, equivalent in absorption to the absorbing gas (assuming Beer's law). It is calculated by the equation, L = Pressure/76. The results are arranged in order of increasing "L." The term absorption limit will be made clear below.

The absorption spectra of hydrogen bromide and iodide appeared continuous, showing no evidence of lines or bands. To determine whether our instrument gives high enough resolution to show the separate partial bands of a possible electronic band system, the following calculations were made. The center of the fundamental infra-red band of hydrogen bromide[7] at 3.9μ, is at wave number $v = 2560$, where $v = I/\text{wave length in cm.}$ Hence the separation of the centers of the partial bands in the ultraviolet band system would be, in wave numbers, approximately $v = 2560$. If L

[7] Imes, *Astrophys. J.*, **50**, 25 (1919).

TABLE I

HYDROGEN BROMIDE

No.	Time, min.	Press. Cm. of Hg	L	Absorp. limit	Tube No.	Plate No.	Notes
1	60	0.9	0.25	2270 Å.	2	28b	4
2	40	4	1.2	2350	2	27c	
3	30	4	1.2	2340	2	28a	4
4	100	2	2.4	2380	3	30c	
5	100	7	8	2430	3	30b	
6	30	37	11	2480	2	26a	
7	65	37	11	2480	2	26b	
8	45	76	12	2460	1	19a	1, 2
9	60	45	13.5	2480	2	38a 39a	5
10	60	45	13.5	2480	2	38b	5
11	60	45	13.5	2480	2	38c 39b	5
12	100	14	16.5	2520	3	30a	
13	100	70	21	2560	2	35a	5
14	90	76	23	2570	2	24a	1, 3
15	100	38	45	2580	3	29c	
16	50	152	46	2520	2	21a	1
17	100	152	46	2520	2	21c	1
18	95	152	46	2600	2	25a	
19	40	152	70	2900	1 and 2	22b	1
20	100	152	70	2800	1 and 2	23b	1
21	100	76	90	2630	3	29a	

TABLE II

HYDROGEN IODIDE

22	100	0.2	0.25	2600 Å.	3	32b	6
23	100	1	1.2	2960	3	32a	6
24	100	20	24	3140	3	31c	6
25	100	43	51	3230	3	31b	6
26	100	120	142	3300	3	31a	6

Notes: 1. Gas not purified by distillation; band spectrum present. 2. Gas was moist. 3. Visible amount of Br_2 present. 4. Absorption limit poorly defined. 5. Absorption tube baked out at 550°. 6. During experiments on HI, a red substance probably HgI_2, formed in tube.

and L' are the wave lengths in centimeters of the centers of two adjacent bands, then $v = (1/L) \times (1/L')$, or $L = L'/(L'V + 1)$. Placing $L' =$ 2500 Å. = 0.000025 cm. (the region in which hydrogen bromide absorbs), the value of L is 2350. That is, the centers of the bands of hydrogen bromide would be separated by 150 Å., or 0.5 cm. on our photographic plates. By a similar calculation it can be shown that the separation of the lines in a partial band would be 1.25 Å. Our instrument would not resolve such lines; but if the lines from two adjacent bands were to merge into a uniform continuous spectrum, each band would have to contain 150/1.25 = 120 lines, of uniform intensity. As this is highly improbable, it appears that hydrogen bromide and iodide have no electronic band absorption spectra.

In the first experiments, a band absorption spectrum was observed extending from 3100 Å. to 2830 Å., approximately, and having 14 flutings in this range. In these experiments the gas was passed over phosphorus pentoxide; the impurity was probably a compound of phosphorus. The fact that this spectrum was eliminated by distilling the gas shows that it was not due to hydrogen bromide. The region of continuous absorption extended from the far ultraviolet (2000 Å.) to a long wave limit, designated as the absorption limit in the table, which depended on the mass of gas traversed by the radiation. This absorption limit was not absolutely sharp, but the transition from apparently complete absorption to apparently complete transmission occurred within a short range of wave lengths (about 30 Å.). The variation of the absorption limit with L can be seen from the tables, and also from the plot in Fig. 2. As the mass of the absorbing gas increases, this limit approaches a limiting value, which is about 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. These values agree with those found by Coehn and Stuckardt,[8] which were about 2650 Å. for hydrogen bromide and 3340 Å. for hydrogen iodide. Varying the pressure from 0.01 atmosphere to 2 atmospheres has no effect

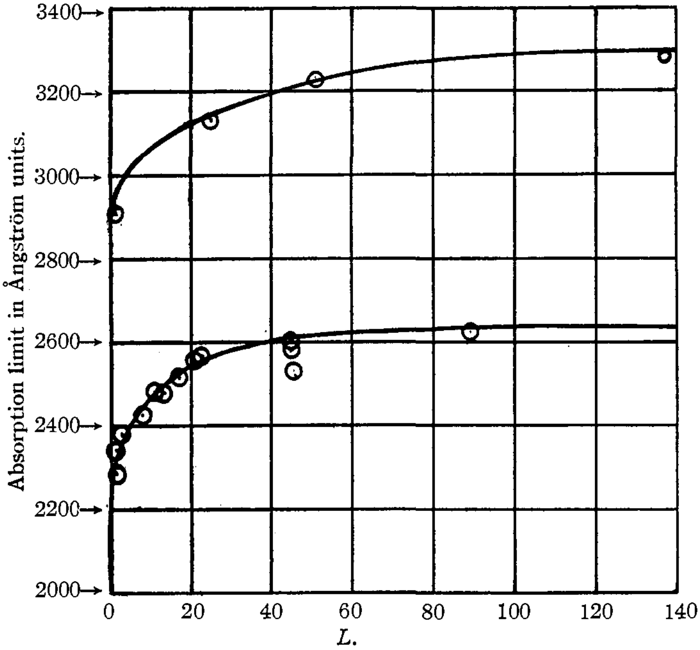

Fig. 2.—Absorption limits and wave lengths.

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

on the nature of the spectrum; nor does it affect the absorption limit, as long as L remains the same. (Compare Nos. 7 and 8; 15 and 18 in Table II.) Varying the temperature from 25° to 400° does not affect the nature and intensity of the absorption, or the absorption limit (compare Nos. 9, 10 and 11 in Table II). These observations on the effect of temperature and pressure also confirm those of Coehn and Stuckardt.

Attempts to Excite an Emission Spectrum of Hydrogen Bromide

A tube similar to the hydrogen tube fitted with aluminum electrodes was filled with hydrogen bromide at 1.5 mm. pressure, and current from the coil passed through it. A blue-red discharge resulted; the electrodes were rapidly attacked, and a white substance, probably aluminum bromide, deposited on the inside of the tube. A plate exposed for 30 minutes showed a continous spectrum and lines in the visible identical with the continuous hydrogen spectrum described above. Superposed on this continuous background in the ultraviolet were several lines due to aluminum, and a group of bands between 2880 Å. and 2760 Å. This group consisted of nine bands, arranged in three sub-groups of three each; the spacing in each sub-group and between sub-groups was fairly uniform. These bands occurred outside the limits of absorption for hydrogen bromide; the carrier was not identified, but it is not considered probable that it was hydrogen bromide.

Another attempt was made to excite an emission spectrum of HBr, using active nitrogen. The usefulness of this method has been pointed out by Mulliken.[9] Our apparatus was essentially the same as his. The nitrogen was prepared by heating air in the presence of yellow phosphorus for some time, and passing the resulting gas through concd. sulfuric acid, a phosphorus pentoxide tube, and a liquid-air trap. The liquid-air trap was found necessary to eliminate a brilliant blue spectrum, probably due to phosphorus, which occasionally appeared in the afterglow tube. The spectrum of active nitrogen then appeared in the afterglow tube. On admitting hydrogen bromide to the afterglow tube, the glow disappeared, and a spectrogram showed that the active nitrogen bands had been suppressed completely, or nearly so, in the region of 3300 Å. to 2000 Å., and in the visible region. The only other effects observed on admitting hydrogen bromide were the appearance of a pair of lines at about 3360 Å., and of a system of four bands at about 4000–3650 Å. Since neither of these lies within the limits of absorption for hydrogen bromide, they are not of interest in connection with its absorption spectrum.

Experiments on the Electrical Conductivity of the Illuminated Gas

As ionization is a possible result of the absorption of radiation, efforts were made to test the electrical conductivity of the illuminated gas. Unfortunately the apparatus available was not sufficiently sensitive to give

[9] Mulliken (a) *Phys. Rev.*, **25**, 119, (b) 259 (1924); (c) **26**, 1 (1925).

conclusive results. The conductivity cell consisted of quartz tube No. 1, down one arm of which were inserted parallel tungsten wire electrodes, about 2 mm. apart, sealed through glass which was sealed directly to the quartz with the aid of a graded seal. The tube was filled with hydrogen bromide gas with precautions as to baking out the tube and purifying the gas. Ultraviolet radiation from a cadmium spark source was focused on the region between the two electrodes, and the electrodes were connected to an electroscope. The rate of leak of the charge of the electroscope was observed with and without irradiation. No conductivity was detected; but the high rate of leakage of the cell itself (due to the fact that the electrodes were sealed through the glass only about 0.5 cm. apart) made it doubtful whether currents of the expected order of magnitude could be detected.

Discussion

This investigation has shown within the limits of the accuracy of the spectrograph used that the ultraviolet absorption spectra of hydrogen bromide and hydrogen iodide are continuous, showing no evidence of band structure. This result may be discussed from two points of view: first, that of the theory of molecular band spectra; and second, that of the mechanism of the photochemical decomposition.

The type of molecular absorption spectrum which has hitherto received most attention consists of a system of bands, and is ascribed to excitation of a molecule which, in its initial and final states, is the same chemical species. The separation of the individual lines in the partial bands is greatest for those molecules having the smallest moments of inertia. Hence, a heavy molecule with a large moment of inertia gives an absorption spectrum which might appear continuous, if the dispersion of the spectrograph were not sufficiently great. In the case of hydrogen bromide and iodide, the theory of band spectra indicates that the separation of the partial bands (expressed in wave numbers) should be approximately equal to the wave number of the zero line of the fundamental vibrational-rotational absorption band in the infra-red region of the spectrum. In the section on experimental results, it has been shown that our spectrograph is capable of resolving bands of this separation, but no bands were found.

Since the spectra appear to be continuous, it is logical to attempt to correlate them with the continuous absorption spectra shown by atoms. The absorption of light is continuous for the principal line series spectra of atoms if the frequency of the radiation is greater than the series limit, which corresponds to the complete ejection of an electron from the atom.[10] In other words, the atom becomes ionized, and the final state of the reaction is not merely an excited atom, but a positive ion and an electron. X-ray absorption spectra are another example of this phenomenon. In

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[10] For discussion and references, see article by Harrison, *Phys. Rev.*, **24**, 466 (1924).

the case of the hydrogen halides, it has been shown by Warburg[2] and others that the absorption of ultraviolet light is accompanied by decomposition into hydrogen and halogen. It is difficult to escape the conclusion that in this case, as in cases of truly continuous absorption, the final state of the absorbing molecule is not the same chemical species as the initial state. Possible final states are (1) hydrogen and halogen atoms, (2) hydrogen halide ion and electron, (3) hydrogen ion and halogen ion. Although sufficient evidence is not at hand to make absolutely sure, it seems most probable that the first of these hypotheses is correct, since in determinations of ionization potentials by electron impact in these gases,[11] no ionization is found until the kinetic energy of the electrons is far greater than the energy of the radiation which produces photochemical decomposition. Our preliminary search for a photo-electric effect in hydrogen bromide gas gave a negative result. Moreover, the energy of the absorbed radiation is greater than that necessary for the decomposition of the gases into atoms. These heats of dissociation for the hydrogen halides are given in Table III, along with the absorption limit and the energy[12] corresponding to this wave length.

TABLE III

COMPARISON OF PHOTOCHEMICAL AND THERMOCHEMICAL ENERGY OF DISSOCIATION OF HYDROGEN HALIDES

Halide	Absorption limit, Å.	Energy of radiation, cal.	$-\Delta H$ (Thermal decompn.), cal.
HCl	2200	130,000	99,500
HBr	2640	108,000	78,300
HI	3320	86,000	68,000

It has been pointed out by Stern and Volmer[3] that the absorption of energy sufficient to dissociate the molecule is not always accompanied by dissociation. For example, the iodine molecule has absorption bands and gives resonance band spectra in the ultraviolet at wave lengths much shorter than that corresponding to the heat of dissociation. The molecules of hydrogen bromide and iodide, however, do not appear to have absorption bands[13] of this type in the ultraviolet but appear to have

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[11] Compton and Mohler, "Critical Potentials," *Bull. Nat. Research Council*, **9**, No. 48 (1924).

[12] This is given by $Nh\nu$, where N is Avogadro's number, h is Planck's constant, and ν is the frequency.

[13] Bands of unusual types have been mentioned by Mulliken [*Phys. Rev.*, **25**, 509 (1925)]. The visible absorption bands of iodine gradually merge and "become lost in a region of apparently continuous absorption which probably means that actual dissociation of the molecule is reached or at least closely approached." Also the emission band of calcium hydride, CaH_2, shows a peculiarity which might be attributed to the instability of the molecule in higher vibrational or rotational excited initial states. In addition Mulliken observes the non-occurrence of band emission spectra for polar compounds of the sodium chloride or silver chloride type. Very recently Barker and Duffendack [*Phys. Rev.*, **26**, 339 (1925)] have looked for emission bands in hydrogen chloride in the region 6000 to 2000 Å. in low-voltage arcs and found none.

continuous absorption, which may account for the absence of emission bands.

As regards the mechanism of the photochemical decomposition, two hypotheses have been advanced. Stern and Volmer[3] postulate that the absorption of light produced an electronically excited molecule as the first step, and that in the second step a collision between the excited molecule and a normal molecule resulted in the formation of a hydrogen molecule and a halogen molecule. In view of the previous discussion, this mechanism must be ruled out, since it was shown that the existence of an electronically excited hydrogen halide molecule is highly improbable.

STERN AND VOLMER MECHANISM

(1) $HX + \text{radiant energy} = HX\ (\text{excited})$. (2) $HX\ (\text{excited}) + HX\ (\text{normal}) = H_2 + X_2$.

Warburg's mechanism assumes that the ultraviolet light decomposes a molecule of hydrogen halide into atoms, and that the hydrogen atom on collision with a normal molecule produces a hydrogen molecule and an atom of halogen. The two halogen atoms then unite to form a molecule. This mechanism is shown in the first three of the equations below.

WARBURG'S MECHANISM

(1) $HX + \text{radiant energy} = H + X$.
(2) $HX + H = H_2 + X$.
(3) $X + X = X_2$.
(4) $HX + X = X_2 + H$.
(5) $H + H = H_2$.

Equations 4 and 5 represent two other possible secondary reactions. Warburg ruled out Equation 4 on the ground that it is accompanied by an increase in free energy, and so could not take place spontaneously; and he pointed out that Equation 5 has a very small probability of occurrence compared with Equation 2, as the concentration of hydrogen atoms is very small. This mechanism explains the fact, brought out by Warburg's experiments, that one quantum of radiant energy decomposes two molecules of hydrogen halide. The data in Table III show that the energy of the light absorbed is sufficient to bring about Reaction 1, and Warburg showed that Reactions 2 and 3 would be spontaneous. It has been pointed out above that the nature of the absorption spectra indicates such a mechanism, at least as regards the primary reaction. Although Warburg put forward his mechanism before the theory of band spectra had received its great development, no facts have been discovered which disagree with it. Nevertheless, the evidence for it is only circumstantial, and definite proof must await the development of methods of detecting small amounts of hydrogen and halogen atoms, whose duration of existence is probably very short.

Two other possible mechanisms suggested themselves, but were found not to be consistent with the experimental results. The first of these assumed the presence in the gases of polymerized molecules, such as are known to exist in hydrogen fluoride. The absorption spectra of such molecules would possibly appear continuous. Absorption by a double molecule could conceivably produce directly a molecule each of hydrogen and halogen, thus accounting in a simple way for the decomposition of two molecules of HX by one quantum of radiation. If this were the case, however, it would be expected that the absorption would be a function of the temperature and the pressure, since increasing the temperature and decreasing the pressure would both tend to bring about the dissociation of the double molecules. No effect of temperature or of pressure on the absorption was observed by Coehn and Stuckardt, by Warburg, or by ourselves. Photographs of the absorption at 25°, 250° and 400°, on the same plate, keeping the length and conditions of exposure the same (Plates No. 38 and 39, Table I, Nos. 9, 10 and 11) showed no appreciable difference in the nature, limit and intensity of the absorption. Coehn and Stuckardt obtained similar results, and Warburg found the absorption coefficient for the wave lengths he used constant with varying pressure. This mechanism was, therefore, dismissed as improbable. The second possibility was that hydrogen halide molecules are adsorbed on the surface of the quartz vessel, and that this adsorbed film is responsible for the absorption of light and the resultant photochemical decomposition. An adsorbed film, however, would be affected by changes of temperature and pressure in much the same way as polymerized molecules. The above remarks in regard to absorption coefficient also rule out this possibility.

Our conclusions regarding the mechanism of the reaction are as follows. The experiments described, with the aid of the quantum theory of spectra, support the postulate that this is a case of dissociation of a molecule into atoms by the direct action of ultraviolet light. The facts that the absorption spectra are apparently continuous, that two molecules of halide are decomposed per quantum of radiation absorbed, and that the energy of the absorbed radiation is sufficient to produce decomposition of the hydrogen halide molecule into neutral atoms, are strong circumstantial evidence in favor of Warburg's original mechanism for the photochemical decomposition of the hydrogen halides.

Summary

1. Ultraviolet absorption spectra of carefully purified gaseous hydrogen bromide and hydrogen iodide have been photographed at various temperatures and pressures, using a continuous spectrum from a hydrogen discharge tube as a source of radiation.

2. Attempts were made to excite an emission spectrum of hydrogen bromide in the ultraviolet, with an electric discharge through the gas, and with active nitrogen. No emission spectrum which could be attributed to hydrogen bromide was found.

3. An unsuccessful attempt was made to detect photo-electric conductivity in hydrogen bromide gas while illuminated by ultraviolet light.

4. The photographs of the spectra show no band structure,[14] but do exhibit continuous absorption extending from the limit of the quartz region in the ultraviolet to a long-wave limit (absorption limit). This limit has been found to be 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. The data support the hypothesis that a case of molecular absorption has been found in which the function of the radiation is not to produce a band spectrum, but to produce direct photochemical dissociation of the molecule into atoms.

5. Mechanisms for the photochemical decomposition of the hydrogen halides have been discussed. The mechanism of Warburg is consistent with all the evidence.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 96]

THE ADSORPTION OF GASES BY PLATINUM BLACK

BY ARTHUR F. BENTON

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If adsorbed films of gases on solids are in general unimolecular, and if the forces involved are typical valence forces acting between individual molecules in the gas and individual atoms in the solid, then the possibility exists, as Langmuir[1] has pointed out, that the volumes of different gases adsorbed by a given surface may be related stoichiometrically. Thus, each atom in the solid surface might be capable of adsorbing one molecule of certain gases, two molecules of certain others, etc.; in still other cases, two or more atoms of the adsorbent might be equivalent to each molecule of gas. It is evident, however, that these stoichiometric relations could occur only if every atom in the surface of the adsorbent takes part in the process, or at least if the same fraction of the surface is active toward different gases. Pease[2] has shown that this condition is not fulfilled in the case of adsorptions on metallic copper, and Taylor[3] concludes that the same is probably true of contact catalysts in general. Nevertheless, when the forces are particularly powerful, as in the adsorption of numerous gases by platinum,

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[14] Since this manuscript has been written, the absorption spectra of hydrogen bromide at different pressures have been photographed with a spectrograph of much greater dispersion. The photographs show no band structure and the spectra appear continuous. These additional data lend still more support to the assumption that the absorption spectra of the hydrogen halides are truly continuous.

[1] Langmuir, THIS JOURNAL, **40**, 1361 (1918).

[2] Pease, *ibid.*, **45**, 2296 (1923).

[3] Taylor, *Proc. Roy Soc.* (London), **108A**, 105 (1925).