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The Photochemical Reaction between Bromine Vapor and Platinum

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The Purpose and Scope of the Investigation.—The investigation here described was a study of the photochemical reaction of gaseous bromine at low pressures with finely divided solid platinum. The particular object was a comparison of the reactions excited by light absorbed in the discrete bands of bromine, and in the region of continuous absorption, respectively.

Since the thermal reaction was found to be appreciable, it was necessary to find the interdependence of this and of the photochemical reaction. This was done by investigating the temperature effect, by varying the light intensity and by studying the effect of the previous history of the platinum–platinum bromide surface on both types of reaction.

Apparatus and Preparation of Materials

The reaction took place in cylindrical glass cells, of diameters 1.8 cm. and lengths 3.5 and 5.5 cm., respectively, the cylindrical walls of which were coated with platinum. The light was admitted to the cell through one end which was closed by a very thin and nearly flat window. Attached to the cells were side-arms containing quartz fiber gages which were used for measuring the pressures (see E of Fig. 1). The fiber gages were calibrated with bromine vapor at various pressures which were obtained by holding a side-tube of the cell containing a little solid bromine at fixed temperatures. These temperatures were obtained by maintaining solid carbon dioxide, moistened with acetone, at reduced pressures. The calibration depended then on a knowledge of the vapor pressures of bromine and of carbon dioxide at various temperatures, data for which were obtained from the "International Critical Tables" and Landolt-Börnstein, respectively. This method of obtaining low temperatures was used owing to the difficulty of obtaining satisfactory fixed points in the temperature range desired, but was found reliable by comparison with a few fixed points.

To cover the walls of the cells with platinum they were first thinly coated with concentrated platinic chloride solution, then dried and heated to a dull red. The resulting platinum was in a finely divided state.

The arrangement for filling the cells with bromine is shown in Fig. 1. The system was first evacuated while the side-tube A, which contained C. P. cupric bromide, was gently heated to expel moisture. Then A was more violently heated and the bromine expelled was condensed in B, which was cooled with a carbon dioxide bath. The cooling bath was then transferred to C, in which the bromine was recondensed, after which the tubes A and B were sealed off from the system at X. Meanwhile the cell was baked out in an oven and when this operation was completed the greaseless magnetic stopcock D was closed and the cell allowed to fill with the vapor of bromine in equilibrium with the solid in C which was at the temperature of solid carbon dioxide at one atmosphere pressure (−79°).

The light source was a 500-watt projection lamp operated on 110 volts. The intensity of such a lamp remained constant for as long as fourteen hours as measured by a Weston photronic cell with a milliameter. The light was condensed with a large lens, passed through the window and focused on the far end of the cell. In some experiments the cross section of the light beam was reduced by placing a diaphragm at the cell window and since the beam was convergent it did not exceed its initial width. The various filters used were placed between the lens and the cell. If a screen was to be used for reducing the light intensity it was placed at the lens.

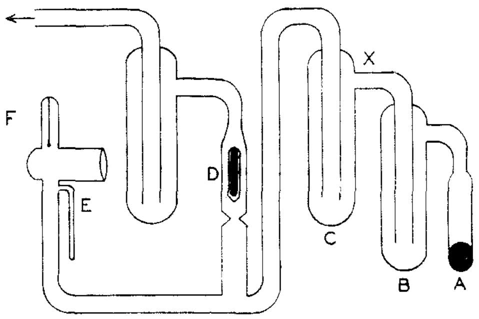

Fig. 1.—Apparatus for filling the cell with bromine.

For studying the effect of light of different spectral regions the following filters were used. To exclude light in the region of continuous absorption of bromine a thickness of 1.1 cm. of 0.1 molal potassium dichromate was used. This removed light of wave length shorter than 5300 Å., the convergence limit of the bromine bands in the visible being at 5100 Å. To exclude light in the region of discrete absorption, cupric ammonium sulfate was used to cut off the green at about 5000 Å.

To reduce the intensity of illumination by a definite amount a screen of fine meshed brass was used, first heated in a flame to cut down the shine. The transmission was determined by using a calibrated Weston photronic cell and a milliameter.

In the experiments made at room temperatures no thermostat was used. The temperature variation never exceeded two degrees and usually was less than one degree. At 0° the cells were surrounded by a mixture of finely chopped ice and water in a large battery jar. The filters in this case were cemented on the outside of the jar by means of sealing wax or a beeswax–rosin mixture.

Conditions of the Experiments

Most of the experiments were started with the same pressure of bromine in the cell, a pressure somewhat less than corresponding to the vapor pressure of bromine at −79°. It was found that after the reaction had proceeded the cell could be regenerated by decomposing the platinum bromide formed by heating the cell gently in a smoky flame, without producing any apparent effect on the reactivity of the surface. The thermal reaction and the combined thermal and photochemical reactions were studied under a variety of conditions which for simplicity in future reference will be designated as follows. (A) The thermal reaction was followed to low pressures. (B) The combined reaction was followed to low pressures. (C) A period of combined reaction was continued until the pressure fell to some definite value, which was followed by a period of darkness: (a) both periods carried on at 25°; (b) period of combined reaction carried on at 0 or −10° and period of thermal reaction at 25°. (D) A period of thermal reaction was followed by a period of combined reaction.

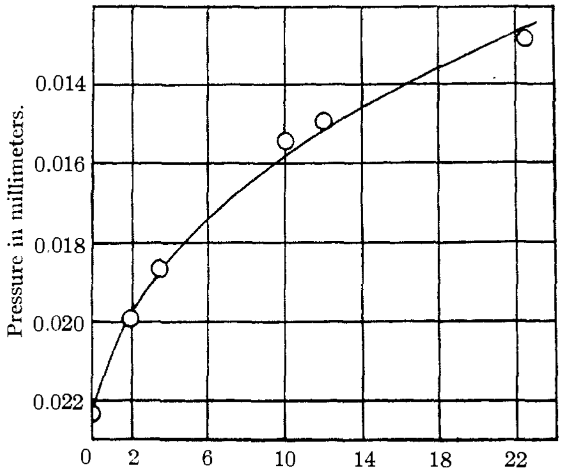

Fig. 2.—The course of the thermal reaction. The circles represent the experimental points and the curve the integrated expression.

Description of Experimental Results

I. The thermal reaction was followed over periods of twenty-four hours in three cells differing somewhat in thickness of platinum coating and in length. It was found that the thermal rates of reaction increased with the thickness of the platinum layer. The thermal reaction of one cell was studied at 0° and the initial rate at this temperature was found to be 51% of its value at 24°.

The dependence of the thermal reaction rate on the pressure was found to be very well represented by the expression

$$-dp/dt = K_1p/(K_2 - p)$$

as is shown in Fig. 2, where the circles represent measurements on one of the cells and the continuous curve was calculated from the integrated expression. Unfortunately the pressure gage of one cell broke before it was calibrated, but since the damping of vibration had been measured when the bromine was frozen out with liquid air, it was possible from this constant to obtain quantities proportional to the pressure from the relation: $D = C + Kp$ where D is the damping of the reciprocal of the time necessary for the amplitude of the vibration to decrease by one-half its original value, and C is the damping at zero pressure.

II. When the cells were illuminated the reaction was found to proceed much more rapidly than in the dark. The course of the combined reaction was studied under a variety of conditions in which the temperature, the light intensity and the spectra region of the exciting light were varied. It was found that the reaction followed a course represented by an equation of the same form as that for the thermal reaction but with different constants, as is shown in Fig. 3.

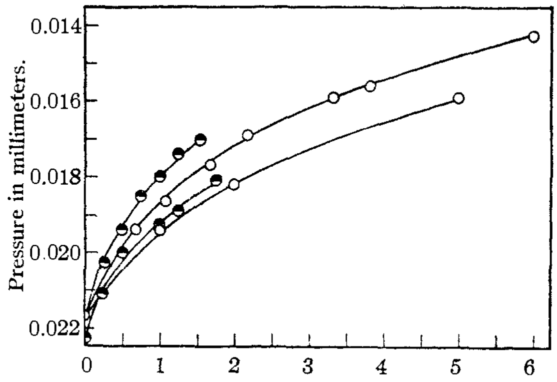

Fig. 3.—The course of the combined reaction under four conditions of illumination: ○, yellow light reactions 25°; ◓, blue light reactions 25°.

(a) In order to compare the temperature dependence of the combined reaction with excitation in the continuous and discrete absorption regions, respectively, the pressure decrease was followed at 25 and at 0° with blue and yellow light. The measurements were somewhat complicated by an increase of adsorption of the bromine at the lower temperature. However, this effect was small and could be corrected for.

(b) The effect of light intensity on the combined reaction was investigated by experiments in which the intensity used in the previous measurements was reduced by a known amount. These experiments were also made using both blue and yellow light.

(c) Further experiments were made with various light intensities which, however, were not measured. From these it appears that reactions excited by blue and yellow light, respectively, can be made to follow courses which are indistinguishable by choosing appropriate light intensities.

(d) In order to investigate the effect of illuminating the bromine vapor at various distances from the platinum, a pencil of light was used of considerably smaller cross section than that of the cell. In some cases this was passed through the center of the cell parallel to the axis and in others was allowed to pass near the inner wall of the cell. The rate of the combined reaction was found to be independent of the position of the beam although in the one case the vapor in the immediate proximity of the wall was illuminated and in the other case the nearest illuminated portion was about 4.5 mm. from the platinum.

III. Under the conditions of C(a) the rate at any given pressure during the second stage (thermal reaction) was apparently the same as at the same pressure when the dark reaction was studied without previous illumination, for cases where moderate illuminations were used and for the cells with thin layers of platinum. In other words, the thermal reaction subsequent to a combined reaction is dependent on the pressure and not on the previous history of the surface for the above cases, as is shown by curves A and C in Fig. 4. The continuous curves are those which were found to fit the data for the thermal reaction after illumination; the points represent measurements on the thermal reaction after illumination, the initial point being the pressure at which illumination was stopped.

For light intensities approximately four times those used above and especially under the conditions of C(b) considerably higher rates were found in the subsequent thermal reactions as is shown by curves B, D and E in Fig. 4.

IV. Under the conditions of D the rate at any definite pressure p during the combined reaction was the same as it would have been if the reaction had been carried out under the conditions of B. This was true for all the cells tried and evidently means that the combined reaction is independent of the previous history of the surface as far as thermal reactions are concerned.

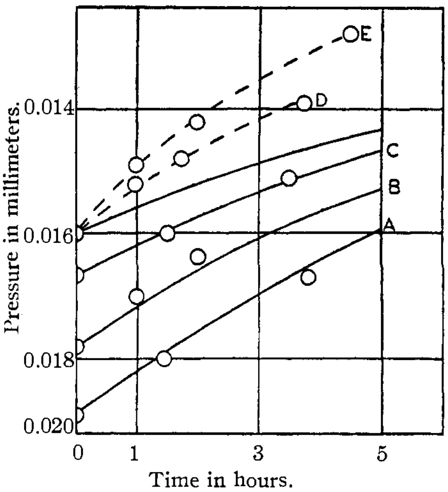

Fig. 4.—The effect of illumination on the subsequent thermal reaction. The continuous curves correspond to the thermal reaction without previous illumination while the points correspond to the thermal reaction after the following illuminations: A, one hour at 25° with yellow light; B, one-half hour at 25° with intense white light; C, one hour at 25° with blue light; D, one hour at 25° with intense white light; E, one hour at 0° with intense white light.

Discussion

As stated above, it was found that the data for both thermal and combined reactions were well fitted by the empirical expression

$$-\frac{dp}{dt} = \frac{K_1 p}{K_2 - p}$$

the constants in which were evaluated from the experimental data by the method of least squares. Various attempts were made to find mechanisms which would lead to this or an equally satisfactory rate expression, but they were all unsuccessful. It may be of interest to note that the denominator of the rate expression can also be written $K_2' + (p_0 - p)$, which suggests an inhibiting effect of the reaction products. It should be noted that the thermal reaction cannot be accounted for simply by collisions of bromine atoms with the platinum surface since their concentration is far too small.

Since no satisfactory mechanisms were found which led to expressions fitting the data, it is not possible to say definitely to what extent the thermal and photochemical reactions can be considered as independent of each other. Nevertheless, certain facts indicate that there are two types of reaction. The acceleration of the reaction by illumination must, at least in the case of blue light, be caused by an increase in the concentration of bromine atoms, while the thermal reaction cannot be due in any appreciable part to collisions of bromine atoms with the walls, as the number of such collisions is too small by a factor of 10^4. However, it is not completely impossible that both reactions involve very long chains started by bromine atoms. In the investigations on the effect of light intensity it was found that the acceleration of the reaction by either blue or yellow light was proportional to the intensity within experimental error for the cases of moderate illumination and medium platinum layers, as is shown in Table I. From this it appears that the total reaction may be regarded as made up of two parts, a thermal and a photochemical reaction, which, at least in certain cases, are independent of each other.

TABLE I

ΔR_1 is the acceleration of the reaction when illuminated without the screen and ΔR_2 is the acceleration when illuminated with the screen. The ratio of the intensity with and without screen, respectively, is 2.15.

Press.	Thermal rate, mm. per hour	Combined rate, blue light + screen, in mm. per hour	Combined rate, blue light in mm. per hour	$\Delta R_1/\Delta R_2$
0.0210	0.001261	0.003590	0.006646	2.32
.0200	.000848	.002252	.004073	2.29
.0190	.000618	.001595	.002853	2.29
.0180	.000475	.001205	.002143	2.28
.0170	.000376	.0009460	.001675	2.28
		Yellow light + screen	Yellow light	
0.0210	0.001261	0.002937	0.005225	2.38
.0200	.000848	.001829	.002907	2.10
.0190	.000618	.001290	.001951	1.98
.0180	.000475	.0009724	.001429	1.92
.0170	.000376	.0007624	.001100	1.88
.0160	.000307	.0006134	.0008735	1.85
.0150	.000253	.0005022	.0007083	1.83

This fact is expressed in the equation

$$-\frac{dp}{dt} = \frac{K_1 p}{K_2 - p} + \frac{K_3 p}{K_4 - p}$$

where the first term corresponds to the thermal reaction and contains the same constants which were found in measurements on the dark cell. The second term we shall call the photochemical rate in the following discussion, and contains a constant K_3 which is proportional to the light intensity. K_4 is nearly equal to K_2, but it was found that the data are better fitted if they are taken as slightly different. The values of the constants for various conditions will be found in Table II.

TABLE II

PHOTOCHEMICAL CONSTANTS

Blue light reactions					
Without screen Press.	K_3	K_4	With screen Press.	K_3	K_4
0.0200	0.00435	0.0227	0.0200	0.00189	0.0227
.0190	.00435	.0227	.0190	.00190	.0227
.0180	.00436	.0227	.0180	.00190	.0227
.0170	.00436	.0227	.0170	.00191	.0227

Yellow light reactions					
Without screen Press.	K_3	K_4	With screen Press.	K_3	K_4
0.0200	0.00216	0.0221	0.0200	0.00127	0.0226
.0190	.00217	.0221	.0190	.00127	.0226
.0180	.00217	.0221	.0180	.00126	.02255
.0170	.00217	.0221	.0170	.00128	.02265
.0160	.00209	.0219	.0160	.00124	.02245
.0150	.00209	.0219	.0150	.00125	.02255

Thermal reaction	
K_1	K_2
0.000140	0.00233

Although no mechanism has been found for the photochemical reaction, comparisons between the reactions involving blue and yellow light are of interest. It was found that a lowering in the temperature of 25° reduced the initial photochemical rate to 83% of its initial value in the case of blue light and to 81% in the case of yellow light, the difference being smaller than the experimental error. As was shown, the reactions apparently have the same dependence on light intensity and can both be described by the same rate expression. Under the conditions of the experiments there was no apparent difference between the two types of reaction and the same mechanism would describe both. From this it appears that in both cases the initial step involves the production of bromine atoms.

This hypothesis is supported by additional facts. From the experiments in which the bromine vapor was illuminated at different distances from the platinum surface, it is possible to obtain further evidence as to the initial step of the yellow light reaction. In one case the vapor in the immediate proximity of the platinum surface was illuminated while in the other the nearest illuminated portion was about 4.5 mm. from the surface, and the rate of reaction was unaffected.

Although it seemed unlikely that the life-time of the bromine molecules in the state to which they are directly excited by absorption in the region of discrete bands would be long enough to allow such molecules to travel 4.5 mm. without going over to some other state, an experiment was made to verify this supposition. Some studies were made of the fluorescence of bromine vapor at the pressure used in the reaction experiments. The fluorescence was too weak to see but was photographed on supersensitive panchromatic film. A special cell was used to eliminate stray light and the bromine vapor was illuminated with a narrow converging beam of intense yellow light. It was found that the region of fluorescence was well defined and coincided with the region of illumination. From this it is evident that in the yellow light experiment the excited bromine must reach the surface in some other condition than that to which the light directly excites it. Now since the number of collisions between molecules is too small for an appreciable fraction of the excited bromine to be dissociated by them, we are left with two possibilities. The bromine may drop to the excited state which is the upper level of the infrared bromine bands with the emission of infra-red fluorescence. But the life-time in this level, although longer than that of the one to which it was initially activated, as indicated by the weakness of the infra-red bands, is still probably insufficient to allow the activated molecules to reach the platinum surface. In any case it was found that the light in the infra-red which would excite the molecules to this level was photochemically inactive. The remaining possibility, which appears the only reasonable one, is that the molecule after excitation by light absorption passes over to one of the energy states which corresponds to the repulsion of the two atoms at all distances and so spontaneously dissociates. This seems in agreement with such facts as are known about the energy states of the halogens and explains the similarity of the reactions caused by light in the region of continuous absorption and in the region of the discrete bands.

Summary

The thermal and photochemical reactions of gaseous bromine with platinum have been investigated. Although no mechanisms have been proposed, an expression was found that described the course of both reactions.

A comparison of the photochemical reactions using blue or yellow light showed the following similarities: the initial rate of reaction was reduced 18% by a 25° reduction in the temperature, the acceleration of the reaction by illumination was in each case proportional to the light intensity, and with either kind of illumination the reaction followed the same course if appropriate intensities were chosen.

The rate of the yellow light reaction was independent of the distance of the illuminating beam from the platinum surface, while the molecules in the state to which they are directly excited by yellow light absorption are confined to the region of illumination, as was shown by photographs of the fluorescent beam of bromine at low pressures.

It was concluded that the initial step in both the yellow and blue light reactions was the same and that a very appreciable fraction of the bromine molecules excited by light in the visible region of discrete absorption dissociate without collision with other molecules.

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