I. THE SEPARATION OF THE TWO TYPES OF IODINE MOLECULE AND THE PHOTOCHEMICAL REACTION OF GASEOUS IODINE WITH HEXENE

II. THE PHOTOCHEMICAL REACTION BETWEEN BROMINE VAPOR AND PLATINUM

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THE SEPARATION OF THE TWO TYPES OF IODINE MOLECULE AND THE PHOTOCHEMICAL REACTION OF GASEOUS IODINE WITH HEXENE

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Soon after Dennison had deduced from the specific-heat curve that ordinary hydrogen gas consists of a mixture of two types of molecule, the so-called *ortho* and *para* hydrogen, a similar state of affairs in the case of iodine gas was demonstrated by direct experiment by R. W. Wood and F. W. Loomis.[1] In brief, these experimenters found that the iodine bands observed in fluorescence stimulated by white light differ from those in the fluorescence excited by the green mercury line λ 5461, which happens to coincide with one of the iodine absorption lines. Half of the lines are missing in the latter case, only those being present which are due to transitions in which the rotational quantum number of the upper state is an even integer. In other words, in the fluorescence spectrum excited by λ 5461 only those lines appear which are due to what we may provisionally call the "ortho" type of iodine molecule.

It is evident than that by irradiating iodine gas with the green mercury line it is possible to selectively activate molecules of the "ortho" type. Furthermore, as shown by these experiments, a molecule of the "ortho" type has an average life time in this form longer than the time it remains in the activated condition before emitting radiation.

It occurred to one of us that these facts might be made use of in effecting a separation of the two molecular types. If some substance is added to the iodine gas with which only the activated molecules will react, one should be able to get rid of them, leaving only the other type of molecule which does not absorb the mercury line.

Since very little is known about photochemical reactions of gaseous iodine, numerous preliminary experiments had to be made to discover a suitable iodine acceptor. It was desired if possible to find a reaction which involved only the direct addition of an activated iodine molecule onto a double bond. We finally found that iodine activated by green light combines with hexene at a reasonable rate, while the thermal reaction is not troublesome since at low pressures the equilibrium is in the direction of almost complete dissociation. The hexene used was prepared by the dehydration of hexyl alcohol with 80 per cent phosphoric acid. It had a

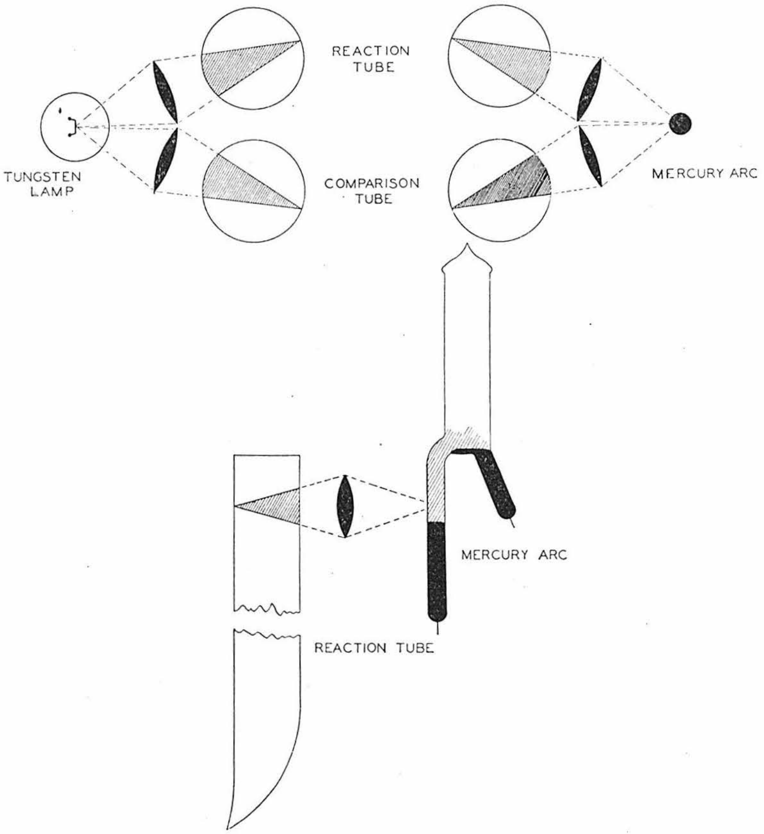

FIGURE 1.

Diagram of the arrangement used in making the fluorescence comparisons boiling point of 68–70°C. and probably consisted principally of the straight-chain form having the double bond between the second and third carbon atoms.

The experiments on the iodine separation were conducted as follows. A tubular vessel of pyrex glass, having at one end a plane window and at the other end a conical "light-trap," was evacuated and then filled with iodine at about 0.17 mm. pressure, and then with hexene at about 6 mm. partial pressure. The tube was then subjected to the intense light from two Cooper-Hewitt glass mercury arcs, using a filter of 0.05 molal potassium dichromate 2 cm. in thickness to cut off all radiations on the violet side of the green mercury line. The lamps were run at considerably below the rated capacity, and were cooled by a blast of air to keep the emission lines as narrow as possible.

After 24 hours about half the iodine was found to have reacted. Tests were then made as follows to determine whether any separation had been effected. A comparison tube was filled with hexene at the same pressure as before, but with the iodine partial pressure adjusted to give the same purple color as that of the reaction tube.

The fluorescence in the reaction and comparison tubes was then compared as represented in the accompanying figure. The light from an intense source was concentrated with strong lenses and passed through the sides of the tubes. On looking down through the plane windows, cones of orange fluorscence were visible. The two tubes were placed side by side, and when equally illuminated comparisons were made of the intensity of fluorescence in the two. These comparisons were necessarily rather qualitative as the fluorescence was weak due to the quenching effect of the hexene.

When the white light from a tungsten lamp was used for excitation, the fluorescence had the same intensity in the two tubes within the experimental error. But when a mercury arc burning at low pressure was used as source of excitation the fluorescence in the comparison tube was considerably stronger. The difference was not great, but quite definite.

The purple color and white-light fluorescence indicate that we have about the same amount of iodine in the two tubes; but evidently there is a difference in certain properties. We believe that we are justified in concluding that in the reaction tube the equilibrium existing in ordinary iodine gas has been materially disturbed, and that an iodine has been produced which contains a higher percentage of the type of molecule which cannot absorb the mercury green line than in the normal mixture.

As to why a more complete separation was not obtained there may be several answers. In the first place it is possible that the rate at which equilibrium between the two forms of iodine is restored is not negligibly small in comparison with the rate of the photochemical reaction. Secondly, the photochemical reaction may not be as simple as one might hope and may involve the production of iodine atoms at some stage. We hope later to investigate the rate and nature of the reaction, as the possibility of distinguishing between two kinds of molecule gives a new tool for this purpose, especially useful in the case of chain reactions.

However, a final experiment, using a more concentrated dichromate filter, indicated that we may be able to improve our results considerably. In this event it is expected to compare the properties of the two types of iodine and to measure the rate at which equilibrium between the two is restored. Some qualitative experiments along this line, which need to be confirmed, indicate that equilibrium is restored rather slowly and several days at least are required. Condensation and re-evaporation of the iodine does not seem to hasten the attainment of equilibrium appreciably, indicating the persistence of the two molecular forms in the solid state.

[1] Wood and Loomis, *J. Frank. Inst.*, **205,** 481 (1928).

THE PHOTOCHEMICAL REACTION BETWEEN BROMINE VAPOR AND PLATINUM

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 cm. 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 gauges which were used for measuring the pressures (see E of Fig. 1). The fiber gauges 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 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 Tables 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 if 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 transfered 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 being 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 at the temperature of solid carbon dioxide at one atmosphere pressure (-79°C).

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 milliammeter. 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 diaphram 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.

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 which 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, using a calibrated Weston photronic cell and a milliammeter.

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°C 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°C. 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 reaction 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 C.

  (b). period of combined reaction carried on at 0°C or at -10°C and a period of thermal reaction at 25°C.

D. A period of thermal reaction was followed by a period of combined reaction.

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 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°C and the inital rate at this temperature was found to be 51 per cent of its value at 24°C.

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

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

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 gauge 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 or the time necessary for the amplitude of the vibration to decrease to one half of 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 sudied under a variety of conditions in which the temperature, the light intensity and the spectral 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. 4.

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°C and at 0°C. 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 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 3. The continuous curves are those which were found to fit the data for the thermal reaction without previous illumination; the points represent measurements on the thermal reaction after illumination, the inital 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. 3.

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 reaction are concerned.

Discussion

As was 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 as $K' + (P_0 - P)$ which suggests an inhibiting effect of the reaction product. 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 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.

This fact is expressed in the following 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.

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 twenty five degrees 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 reactions 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. This fact puts a severe limitation on the ways in which activated bromine may reach the surface. The average life time of a molecule in the state to which it is directly activated by light absorption is almost certainly much shorter than the time required to travel 4.5 mm., while on the other hand the mean free path is too great to allow of its dissociation by ordinary collisions with other molecules. Thus we are left with two possibilities. The bromine may drop to the excited state which is the upper level of the infra-red 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 excited, as indicated by the weakness of the infra-red bands, is still probably insufficient to allow activated molecules to reach platinum surface. In any case it was found that the light in the infra-red which would excite the molecule to this level was photochemically inactive. The remaining possibility, which appears the only one probable, is that the molecule passes over to one of the energy states which corresponds to 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.

Table I

Rate of Combined Reaction in mm. per Hour with Blue Light

Pressure in mm.	Combined Rate	Combined Rate with Screen	% Reduction in Photochemical Rate Due to Screen
0.0210	0.006646	0.003590	43
0.0200	0.004073	0.002252	43.6
0.0190	0.002853	0.001595	43.7
0.0180	0.002143	0.001205	43.8
0.0170	0.001675	0.000946	43.9

Rate of Combined Reaction with Yellow Light

0.0210	0.005225	0.002937	42
0.0200	0.002907	0.001829	47.6
0.0190	0.001951	0.001290	50.4
0.0180	0.001429	0.0009724	52.1
0.0170	0.001100	0.0007624	53.3
0.0160	0.0008735	0.0006134	54.1
0.0150	0.0007083	0.0005022	54.7

Rate of Thermal Reaction

0.0210	0.001261
0.0200	0.000848
0.0190	0.000618
0.0180	0.000475
0.0170	0.000376
0.0160	0.000307
0.0150	0.000253

The percent reduction in light intensity due to screen equals 46.5.

Table II

Constants for the Photochemical Reaction

Blue Light Reactions

	Reaction 1		Reaction 2	
Pressure	K_3	K_4	K_3	K_4
0.0200	0.00435	0.0227	0.00189	0.0227
0.0190	0.00435	0.0227	0.00190	0.0227
0.0180	0.00436	0.0227	0.00190	0.0227
0.0170	0.00436	0.0227	0.00191	0.0227

Yellow Light Reactions

	Reaction 1		Reaction 2	
0.0200	0.00216	0.0221	0.00127	0.0226
0.0190	0.00217	0.0221	0.00127	0.0226
0.0180	0.00217	0.0221	0.00126	0.02255
0.0170	0.00217	0.0221	0.00128	0.02265
0.0160	0.00209	0.0219	0.00124	0.02245
0.0150	0.00209	0.0219	0.00125	0.02255

Constants for the Thermal Reaction

K_2	K_7
0.0233	0.00014

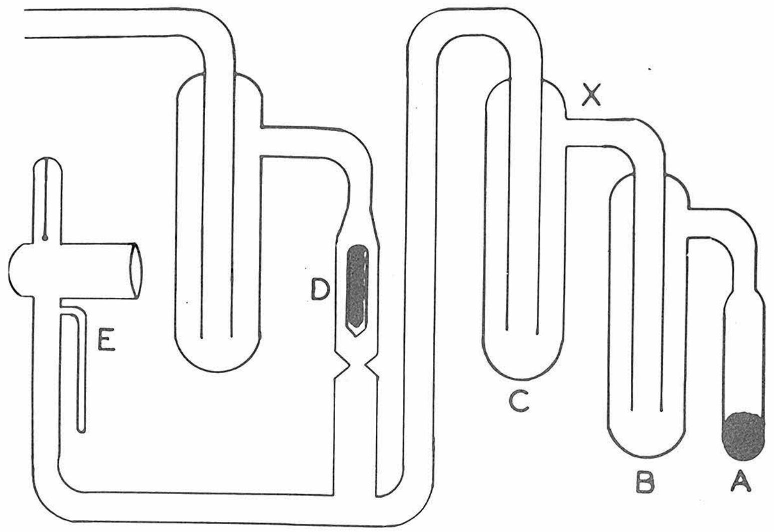

Figure 1

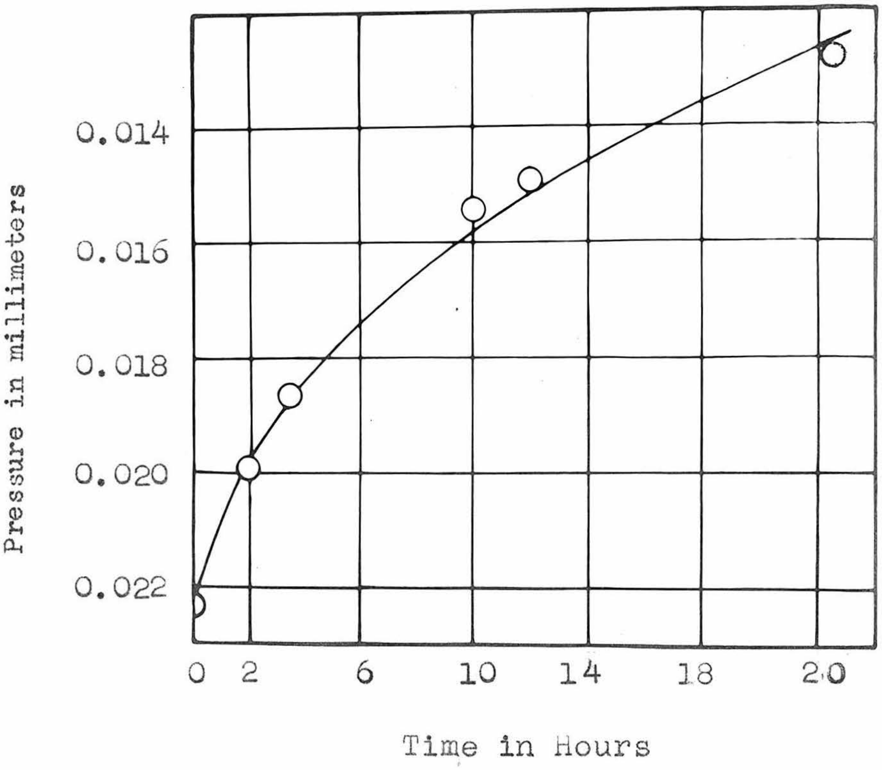

Figure 2.

The course of the thermal reaction.

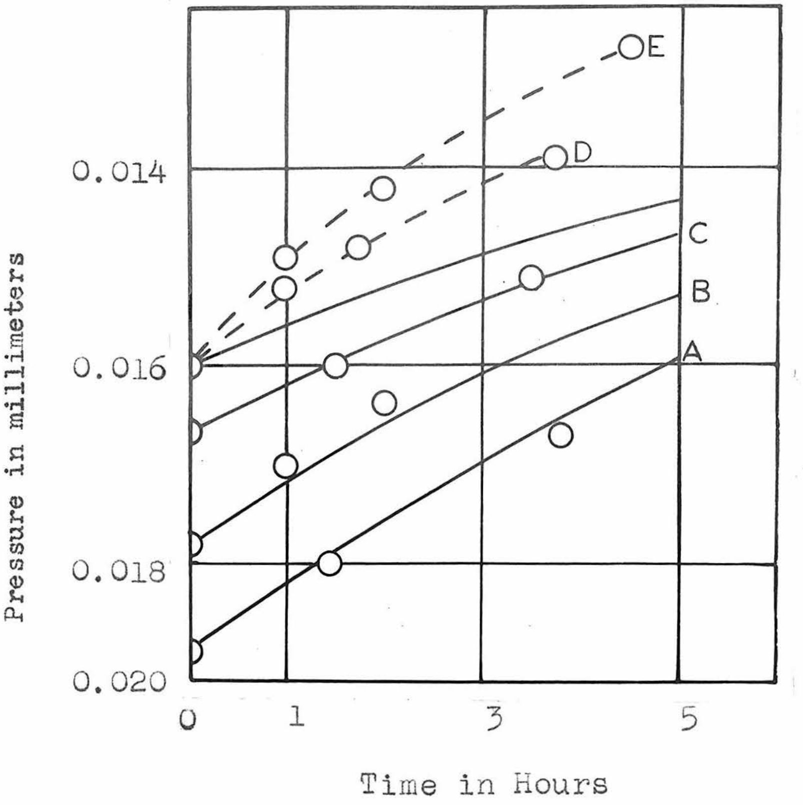

Figure 3.

The course of the thermal reaction after illumination.

The points on the above curves correspond to the thermal reaction after illumination, while the continuous curves correspond to the thermal reaction alone.

A. The cell was illuminated for one hour at 25 C with yellow light.

B. The cell was illuminated for one half hour at 25 C with intense white light.

C. The cell was illuminated for one hour at 25 C with blue light.

D. The cell was illuminated for one hour at 25 C with intense white light.

E. The cell was illuminated for one hour at 0 C with intense white light.

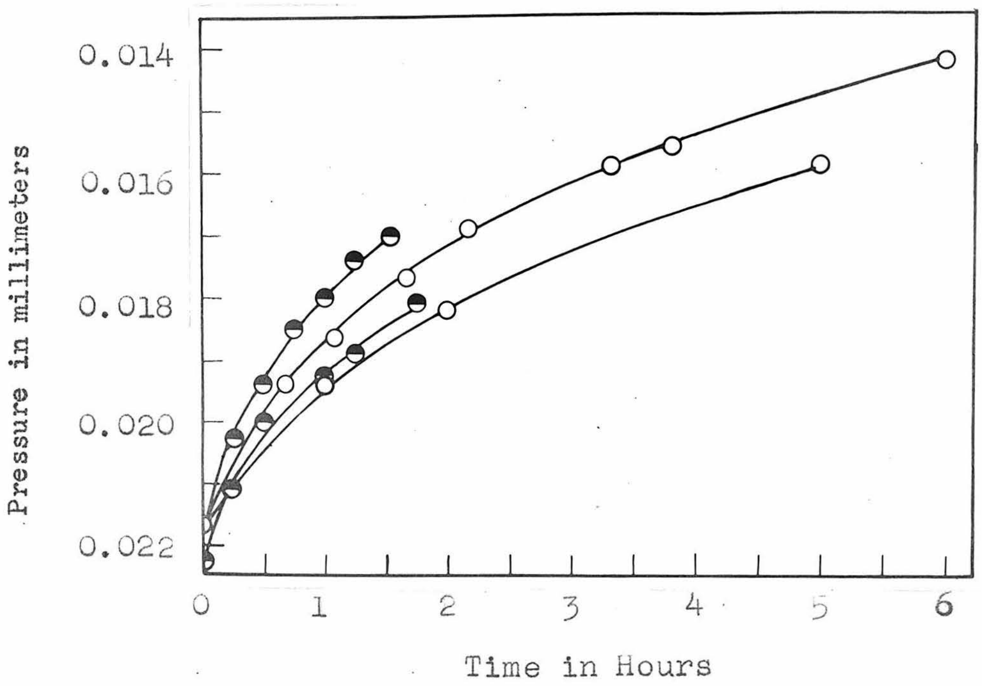

Figure 4.

The course of the combined reaction for blue and yellow light.

The white circles correspond to the yellow light reaction, and the half black circles correspond to the blue light reaction. The continuous curves in each case were obtained from the integrated reaction rate expression.