[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PHOTOCHEMICAL DECOMPOSITION OF AZOMETHANE

BY HERMAN C. RAMSPERGER[1]

RECEIVED OCTOBER 31, 1927 PUBLISHED JANUARY 5, 1928

The rate of the thermal decomposition of azomethane has been shown to be unimolecular over a small range of high pressures,[2,3] but the constant becomes somewhat smaller at low pressures.[4] This effect is expected if the reaction is due to molecules activated by collisions with other molecules. Rice and the author[5] considered two such theories and derived equations showing the way in which the rate would fall off with decreasing pressure. These have been applied to the decomposition of azomethane,[6] and the experimental values check one of the theories (Theory II) quite well. There is the possibility that in the case of azomethane there may be a chain reaction, especially since the reaction is certainly exothermic, as is indicated by the explosive nature of the gas.[7] This would require quite a different explanation of the reaction rate as, for example, that postulated by Christiansen and Kramers.[8]

The length of a chain reaction can be determined in the case of activation by light by measurements of the photochemical efficiency. Activation by light may produce molecules with a more definitely specified total energy and energy distribution than is the case with thermally activated molecules. This would be especially true if the light were very nearly monochromatic and if the molecule had an easily resolvable band spectrum, for then absorption of one particular spectrum line would determine both the initial and final states of the molecule. Thermally activated complex molecules would not be greatly restricted as to total energy or energy distribution. If, however, it is sufficient for reaction that a molecule have a certain minimum total energy independent of the nature of this energy, then we should expect the reaction to be similar for these photochemically activated molecules. If it is necessary that a particular degree of freedom obtain a minimum of energy, as in Theory II of Rice and Ramsperger,[5] and this energy may be obtained from any other degrees of freedom by repeated redistribution within the molecule between collisions, then it will not matter in what part of the molecule the light energy

---

[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, 49, 912 (1927).

[3] Experimental work now in progress shows that the range over which the reaction is unimolecular is greater in the case of other azo compounds, as for example azo*iso*propane.

[4] Ramsperger, *ibid.*, **49**, 1495 (1927).

[5] Rice and Ramsperger, *ibid.*, **49**, 1617 (1927).

[6] Rice and Ramsperger (forthcoming).

[7] Thiele, *Ber.*, **42**, 2575 (1909).

[8] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

was absorbed.[9] Nevertheless, the energy of a photon, or light quantum, of the light used (77,800 cal.) is so much larger than the heat of activation (51,200 cal.) that if the length of any reaction chain were a function of the energy in excess of the activation energy, the photochemical chain reaction would be even longer than the thermal one. It will be found experimentally that only about two molecules decompose for each photon absorbed. Evidence will be presented to show that the thermal decomposition also is probably not a long chain reaction.

The Absorption Curve

Liquid azomethane has a very slight yellow color. The gas would therefore be expected to have a strong absorption band in the near ultraviolet. Quantitative absorption measurements were made by the method of Ramsperger and Porter.[10]

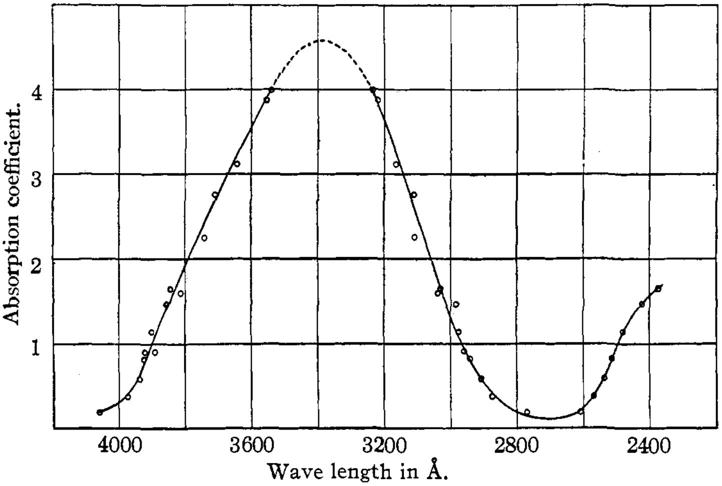

Fig. 1.—Ultraviolet absorption curve of azomethane.

Light from a quartz mercury arc was passed through a quartz cell 60 cm. long containing azomethane and was photographed with a Hilger quartz spectrograph. On the same plate another photograph was taken of the same source of light through the same cell evacuated and through a copper gauze screen of known absorption. The blackening of the plate is the same in the two photographs at any wave length for which the particular screen and the azomethane gas have the same absorption. Positions of equal intensity were determined by the method given by Ramsperger and Porter.[10] Absorption coefficients were calculated by the relation $I_t/I_0 = 10^{-ecd}$, where I_t/I_0 is the fraction of light transmitted, e is the molecular absorption coefficient, c the concentration in moles per liter and d the length of the cell (60 cm.). There was no evidence of a band spectrum. The results are given in Table I and plotted in Fig. 1.

---

[9] It is possible also that the absorption of light energy will involve some energy states that do not occur at all in molecules activated thermally, and these may not have the same effect in producing reaction.

[10] Ramsperger and Porter, This Journal, **48**, 1267 (1926).

TABLE I

POINTS OF EQUAL INTENSITY (ÅNGSTRÖM UNITS)

Screen no.	Light transmitted by screen, %	Expt. 1 P = 9.01 cm. T = 20.5°	Expt. 2 P = 24.98 cm. T = 21.0°	Expt. 3 P = 5.32 cm. T = 21.0°
1	69.3	......	4060 2770 2610	3890 2960
2	48.8	......	3974 2874 2570	......
3	33.1	3815 3040	3938 2908 2538	3710 3112
4	21.2	3738 3108	3925 2942 2515	3555 3220
5	11.5	3645 3166	3900 2976 2480	......
6	6.3	3540 3236	3856 2984 2426	......
7	4.4	......	3845 3032 2374	......

Monochromatic Light

The source of light for the decomposition experiments was a vertical 220-volt Cooper-Hewitt mercury arc. An attempt was made to use a Hilger Monochromator, but the intensity of the three lines, 3663, 3654 and 3650 Å. was hardly great enough to permit accurate measurements of the decomposition. A filter was therefore used. It was a modification of the one used by Eggert and Noddack.[11] The filter cell was 5 cm. in diameter and 4.5 cm. long. A blue cobalt glass was sealed on each end of the cell in place of the ammoniacal copper sulfate solution used by Eggert and Noddack. A solution of 0.10 g. per liter of phenosaphranine was circulated through the cell at the rate of 50 cc. per hour. The transmitted light consisted almost entirely of the three lines mentioned above. This was proved by photographing the transmitted light with a quartz spectrograph. The strong blue line at 4046 Å. and several weak lines closer to the three ultraviolet lines were each about as dense as the strong line 3663 Å. was with an exposure only one-thousandth as long. No other lines were visible on the plate. However, this filter transmitted some deep red and infra-red light which had to be corrected for in the energy measurements.

Apparatus

The apparatus was arranged in the following order: the mercury arc, a quartz lens two inches in diameter and three inches in focal length, the filter cell described above, a camera shutter and then either a linear thermopile in case energy measurements were made or the quartz reaction vessel containing azomethane. The mercury arc had a metal plate attached which was as wide as the arc and 1.5 cm. high. The lens was placed so as to form a sharp image of the arc 1.85 cm. high. The thermopile was a ten-junction Coblentz linear thermopile, the slit of which was a little less in height than the image of the arc and could either be placed with the sharp image of the arc on the thermopile surfaces or could be swung through 90° to face a Bureau of Standards standard of radiation lamp exactly two meters distant. This thermopile could be moved with a screw device back and forth across the image of the arc. The quartz reaction cell was 3 cm. in diameter and 9.13 cm. long. It could be placed so that the entire beam of light came well within the cell.

Energy Measurements

A high sensitivity, low resistance, D'Arsonval galvanometer was used to measure the thermopile current. With a scale at 3.5 meters from the galvanometer large deflections were obtained. When very large deflections were to be measured a resistance of 3 ohms was shunted across the

---

[11] Eggert and Noddack, *Z. Physik*, **20**, 299 (1924).

galvanometer. This reduced the deflections by an experimentally determined factor of 2.61.

The general method of determining the radiation density was to move the thermopile across the image of the arc, taking readings at every millimeter near the center of the image where the radiation density was very great and every 2 mm. on the edges of the image. These deflections (properly corrected for infra-red radiation) were plotted on coördinate paper as ordinate and the position of the thermopile as abscissa. The area under this curve was determined. This area multiplied by the radiation density per sq. mm. per sec. per cm. deflection, as determined by calibration of the thermopile galvanometer arrangement against the standard lamp and then multiplied by the height of the image in mm., gives the total radiation of the three mercury lines falling per second on the cell.

The actual procedure was as follows. Before each experiment the arc was allowed to become constant, which required at least thirty minutes after starting. The thermopile was evacuated and the mercury diffusion pump was kept running during the entire experiment, as it was noticed that the thermopile sensitivity was more constant if pumping was continuous. The thermopile-galvanometer arrangement was calibrated by means of the radiation standard supplied by the Bureau of Standards and according to the specifications supplied with it. Usually about five readings were made which were constant to about 1%. The calibration was repeated after the energy measurements were complete and an average was taken. The deviation from the average was usually about 1%.

Readings were started on one edge of the image of the arc. Three readings were made at each position of the thermopile, (1) with the shutter closed; (2) with the shutter open and a sheet of "Crookes A" glass and a sheet of fused quartz in the path of the light; (3) with the shutter open and only the sheet of quartz in the path. The quartz sheet was similar to the front window of the reaction cell and the radiation passing through this sheet would correspond to the radiation entering the cell. The "Crookes A" glass absorbs all of the ultraviolet radiation, as was proved by photographing the ultraviolet spectrum with a sheet of "Crookes A" glass in the light path. It was also found that not all of the radiation passing through the filter cell was absorbed by the "Crookes A" glass and that the per cent. of this infra-red radiation varied for different parts of the image of the arc but was usually 20 to 25% of the total radiation. A second sheet of "Crookes A" glass was found to transmit 75% of the radiation transmitted by the first sheet. The galvanometer deflection corresponding to the three ultraviolet lines can then be calculated by the equation (3–2)—(2–1)/3.

The deflections calculated in this way for the first energy determinations of Expt. 3 are plotted in Fig. 2. The area under this curve is 1826 mm. deflections. The standard lamp when burning on 0.350 ampere gives an energy density of 8.4 ergs per mm.^{2} per sec. at two meters' distance, and gave under these conditions a deflection of 19.3 cm. at the beginning and 18.9 cm. at the end of the energy determination. The energy density per mm. height of image is therefore $(1826 \times 8.4)/(19.1) = 803$ ergs per sec. The arc is uniformly intense from top to bottom and even if there were slight variations, the thermopile covered most of the height and would have recorded an average energy density. The height of the image was 18.5 mm. which gives as the total energy 803 × 18.5 = 14,860 ergs per sec. There is yet a possible correction due to a greater reflection or absorption of the ultraviolet light as compared to that for the light of the standard lamp by the fluorite window of the vacuum thermopile. The difference in reflection is negligible. There are no data on the absorption of different wave lengths by fluorite, but this is certainly only a small correction and will not be considered.

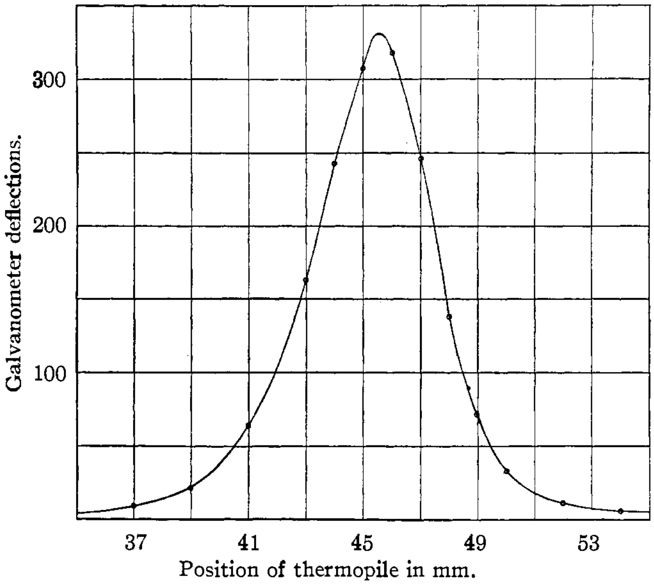

Fig. 2.—Energy distribution curve.

Decomposition of Azomethane

Four experiments were made at a temperature of 20° and at initial pressures from 0.1207 cm. to 25.74 cm. The pressure measurements of Expts. 1 and 2 were made on a closed tube manometer and in Expts. 3 and 4 a small McLeod gage was used. In all of these experiments the total number of moles decomposed is readily calculated from the total volume and the change in pressure, since it had been shown[2] that the decomposition is largely by the equation $CH_3NNCH_3 = N_2 + C_2H_6$. The final pressure actually is 2.04 times the original pressure, due to a small amount of side reaction. The number of moles decomposed is therefore given by the equation

$$N = \frac{\Delta PV/1.04}{RT}$$

where ΔP is the increase in pressure and V is the total volume.

The volume of the quartz cell was 67 cc. and the connecting tubing to the top of the mercury surface had an average volume of 14 cc. in Expt. 1 and 12 cc. in Expt. 2. The low pressure Expts. 3 and 4 were made with apparatus similar to that used in a previous research.[3] The volume of the cell and the tubing connecting it to the mercury trap was 70 cc., the volume of the trap and tubing connecting it to the McLeod gage was 2.8 cc. and the volume of the gage was 8.9 cc. The total volume was therefore 81.7 cc.

The Fraction of Light Absorbed

The fraction of the light absorbed can be calculated from the absorption coefficient, knowing the length of the cell and the pressure of azomethane in the cell. Diffusion will be sufficiently rapid to give the same partial pressure of azomethane throughout the reaction cell, but practically no diffusion will occur into the tubing leading to the manometer in Expts. 1 and 2. The partial pressure of azomethane will therefore be less in the cell than in the tubing after some decomposition has occurred. Since only a small part of the azomethane was decomposed, this will make very little difference. However, the correct partial pressure of azomethane in the cell is readily calculated. It is given by the equation

$$P_1 = P_i - \Delta PV/V_1 - \Delta PV_2X_A/1.04V_1$$

where P_i is the initial pressure, ΔP the increase in pressure, V the total volume, V_1 the volume of the cell, V_2 the volume of the tubing and X_A the mole fraction of azomethane entering the tubing from the cell.

This is shown as follows. The partial pressure of azomethane in the manometer tubing at any time t is given by $P_2 = P_i + \Delta PX_A$. X_A is given with sufficient accuracy by the equation $X_A = (P_i - \Delta P/1.04)/(P_i + \Delta P)$ where ΔP is the average of the total increase in pressure at that reading and the previous reading. Let N_1 represent the moles of azomethane in the cell, N_2 the moles of azomethane in the tubing and N the total moles of azomethane at any time t. We have $N_1 = P_1V_1/RT$, $N_2 = P_2V_2/RT$, $N = (P_i - \Delta P/1.04)V/RT$. Also $N = N_1 + N_2$. If now the above value of P_2 is substituted, we obtain the equation given above for P_1. In Expts. 3 and 4 the calculation of the pressure of azomethane in the cell was the same as given in a previous paper.[3] As formerly, P_A' denotes the pressure of azomethane in the cell before the reading with the McLeod gage was made and P_A'' denotes the pressure of azomethane after the reading.[12] The average value of the pressure of azomethane in the cell during each time interval is obtained by averaging the value of P_A'' of one reading and P_A' of the next reading. This is the pressure of azomethane upon which the absorption is based.

The absorption coefficient for light of wave length 3660 Å. is found from the curve of Fig. 1 and to be 3.10. This absorption coefficient was checked by use of the thermopile. The cell filled with azomethane gas for Expt. 1 was placed between the light source and the thermopile. The galvanometer deflection was read, the azomethane was frozen out with liquid air and another reading made. After correcting for the infra-red radiation as in the energy measurements it was found that 63% of the ultraviolet light of the three mercury lines was absorbed. The absorption calcu-

---

[12] The equation for P_{At}'' given on page 1496 of ref. 3 should of course have read $P_{At}'' = P_{At}'P_t''/P_t'$.

lated from the absorption coefficient, the length of the cell (9.13 cm.) and the concentration in moles per liter (0.0141), was 60%. Considering the uncertainty of the corrections this is a good agreement. The absorption has been calculated for each time interval and is based on the absorption coefficient, 3.10, and the average concentration of azomethane in the cell.

In addition to the absorption so calculated, a fraction of the light from the two surfaces of the rear window is absorbed. From Fresnel's formula for the reflection of perpendicularly incident light, that is, $r = \left(\frac{n-1}{n+1}\right)^2$, where n is the index of refraction of quartz for $\lambda = 3660$ Å., approximately 12% of the transmitted light is reflected from these two surfaces. The absorption of this reflected light is calculated as before. Secondary reflections are neglected.

The results of the four experiments are given in Table II.

Table II

Data of Four Experiments

Expt. 1. Average energy density = 14,480 ergs/sec.

Time, hours	P, cm.	P_1, cm.	Av. P_1, cm.	Moles decomposed $\times 10^6$	Ergs absorbed $\times 10^{-7}$
0	25.74	25.74			
			25.42	2.09	3.26
1	26.23	25.10			
			24.80	1.92	3.22
2	26.68	24.49			
			24.23	1.66	3.17
3	27.07	23.97			
			Total	5.67	9.65
	Expt. 2.	Average energy density = 14,400 ergs/sec.			
0	9.60	9.60			
			9.42	1.17	1.63
1	9.87	9.25			
			9.09	1.08	1.59
2	10.12	8.93			
			8.77	1.04	1.54
3	10.36	8.62			
			8.46	1.08	1.50
4	10.61	8.30			
			8.17	0.86	1.45
5	10.81	8.05			
			Total	5.23	7.71

Expt. 3. Average energy density = 14,490 ergs/sec.

Time, hours	P, cm.	P'_A cm.	P''_A cm.	Av. P_A, cm.	Moles decomposed $\times 10^6$	Ergs absorbed $\times 10^{-7}$
0	0.991		1.031			
				1.008	0.165	0.217
1.05	1.031	.986	.981			
				.962	.142	.197

TABLE II (*Concluded*)

Time, hours	P, cm.	P'_A cm.	P''_A cm.	Av. P_A, cm.	Moles decomposed $\times 10^5$	Ergs absorbed $\times 10^{-7}$
2.05	1.066	.943	.939			
				.922	.127	.188
3.05	1.096	.904	.901			
				.869	.239	.356
5.05	1.154	.836	.831			
				Total	.673	.958
	Expt. 4.	Average energy density = 13,880 ergs/sec.				
0	0.1207	....	0.1255			
				0.1205	0.0370	0.048
2.00	.1296	0.1155	.1146			
				.1109	.0271	.044
4.00	.1362	.1073	.1067			
				.1029	.0275	.041
6.00	.1429	.0991	.0985			
				.0957	.0215	.033
7.75	.1480	.0928	.0924			
				Total	.1131	.166

The final result to be calculated is the number of molecules decomposed per photon of light absorbed. This number is given by $\phi = h\nu \times$ moles decomposed $\times$ 6.06 $\times 10^{23}$/ergs absorbed, where $h\nu$ is the energy in ergs of a photon of light of the wave length λ = 3660 Å. The values of ϕ are as follows.

Expt.	1	2	3	4
ϕ	1.91	2.21	2.29	2.22

Temperature Coefficient

An attempt was made to determine the temperature coefficient of the photochemical decomposition. The absorption curve was not appreciably changed at 100°. A very slight deposit was formed on the front window of the reaction chamber. This actually reduced the rate below that at 20°, due probably to the absorption of light by this film. It was found, however, that on changing the gas to 20° the rate in moles decomposed was the same as it was at 100° just before the temperature was changed. Experiments at low pressures would have avoided the difficulty but they were not undertaken owing to lack of time. It seems, however, that the temperature coefficient of the photochemical decomposition is very nearly zero, and certainly not greater than 1.02 for an increase in temperature of 10°.

Discussion of Results

The value of ϕ is practically constant over a 200-fold pressure range and is approximately 2. Expt. 1 is a little lower than the rest, probably because a similar deposit to the one produced at 100° may have formed.

This would be most serious at high pressures and would produce a steady lowering of the rate of decomposition as the experiment progressed, which was actually the case in Expt. 1.

It might be supposed that some molecules would be deactivated by "collisions of the second kind" and that this deactivation would be most serious at high pressures. The constant value of ϕ over this large pressure range would indicate no such deactivation. Either collisions are not effective in deactivating activated molecules, which is not likely, or else they react in a time shorter than the time between collisions at the high pressures. The time between collisions at 25 cm. pressure is about 2×10^{-10} seconds if the diameter of the molecule is taken as 6×10^{-8} cm.

In the case of thermal decomposition we can calculate the ratio of molecules reacting to molecules deactivated by collisions if we accept Theory II of Rice and the author.[5,6] This ratio is given by b_ϵ/aN, where

$$b_\epsilon = \frac{K_\infty \Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} \frac{e^{\frac{\epsilon_0}{kT}}}{(kT)^{\frac{1}{2}}} \frac{(\epsilon - \epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}}, \quad a = 4s^2 \sqrt{\frac{\pi k T}{m}}$$

and N is the number of molecules per cc. T is taken as 290° to correspond to $K = 1.4 \times 10^{-4}$. For the molecular diameter 6×10^{-8} is used. N is calculated for a pressure of 25 cm. and the number of degrees of freedom is 25, this being the value of n required to fit the experimental data; ϵ_0 is 50,600 cal. per mole. If now we take as ϵ 77,800 cal. per mole, which is the energy of a photon of $\lambda = 3660$ Å., we get for the ratio 14/1. This calculation does not allow for the internal energy of the molecule before it absorbs the photon. This energy is of course not known, but the average internal energy of all of the molecules is roughly 5,000 cal. per mole, giving ϵ a likely value of 82,800 cal. The ratio then becomes 47/1. The result of this calculation requires that an activated molecule with this very high energy must react within about 10^{-11} seconds after activation. If the type of activation were the same in the photochemical as in the thermal reaction, then deactivation could seldom occur by collision even at the highest pressures, nor could the molecule be deactivated by radiation of the energy, since the time required for radiation is generally more than 10^{-8} sec. The constant value of ϕ over this large pressure range is the expected result if the type of activation and mechanism of reaction were the same in both photochemical and thermal reactions.

The fact that approximately two molecules are decomposed per photon absorbed may possibly be explained by the energy of a newly formed ethane molecule being transferred to a molecule of azomethane which is then activated. This is only possible because of the large excess of energy in the photon and could not be repeated indefinitely, thus producing a long chain. For example, a gram mole may have 83,000 cal. after the photon is absorbed. At least 20,000 cal. is obtained as heat of the reaction itself.[6] This gives more than 103,000 cal. to be divided between a N_2 gram molecule and an ethane gram molecule. The ethane would get by far the larger portion of this energy if statistical equilibrium between the various degrees of freedom of both molecules exists. It must then impart some 60,000 cal. or more to an average azomethane gram molecule to make its reaction probable. Unless the heat of the reaction is very much higher than 20,000 cal., or the energy of surrounding molecules very great, the third molecule of azomethane in such a chain would not have sufficient energy to react, especially if the pressure were high.

Summary

The photochemical decomposition of azomethane has been studied in order to determine the length of the photochemical reaction chain and to test further certain theoretical interpretations of the unimolecular thermal decomposition.

The quantitative absorption curve for ultraviolet light has been determined from 4060 to 2370 Å. There is an absorption maximum at 3390 Å., with increasing absorption again toward the extreme ultraviolet.

The light used for the decomposition consisted of three mercury lines at about 3660 Å., which were isolated by means of a filter. The total energy falling on the reaction cell was determined by means of a thermopile and the fraction of the light absorbed was calculated from the absorption coefficient.

The decomposition was followed by pressure measurements. Four experiments were made at pressures from 0.1207 cm. to 25.74 cm. Two molecules were found to be decomposed for each photon absorbed in all four experiments.

The temperature coefficient was found to be very nearly zero.

On the basis of Theory II of Rice and the author,[5,6] most of the thermally activated molecules having energies corresponding to the average energy of all of the molecules plus the energy of the photon will react even at the highest pressure. Deactivation by collision seldom occurs, because the life of a molecule is less than the time between collisions even at the highest pressure. A constant value of moles decomposed per photon absorbed is the expected result if the mechanisms of the photochemical and thermal reactions are similar.

The decomposition of two moles per photon absorbed may possibly be explained by the transfer of sufficient energy by a newly-formed ethane molecule to an azomethane molecule to cause it to react.

BERKELEY, CALIFORNIA