no matter by what method one measures association in the liquid phase, one finds that the observed values depend upon the electron-sharing abilities of the radicals concerned. This dependence is in the same direction as that predicted, and found, for association of organic compounds in solution. Hence the contributing factors in each case must be the same, *i. e.*, the presence of doubly covalent hydrogen.

Summary

1. Data are presented which show that the normalizing effect of a solvent is due to the association of the solvent with the solute. This relation was found by studying the behavior in benzene of two compounds together, one, called the solute (*p*-chlorophenol) in fixed concentration, the second, called the solvent (benzaldehyde) in variable concentration.

2. Data are presented which show that the normalizing power of a series of ketones depends in a regular way on the electron-sharing ability of the radicals attached to the carbonyl group.

3. Both the data and the theoretical considerations indicate that the dielectric constant of a solvent has little if any effect on associations due to hydrogen bonding.

AMES, IOWA RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Photolysis of Azomethane

BY C. V. CANNON[1] AND O. K. RICE

Azomethane has been considered particularly adapted to decomposition studies because this reaction is apparently a unimolecular one which has no chain (or else a very short one) and is comparatively free from complicating side reactions. A number of investigators[2] have studied the thermal and photochemical decompositions. Ramsperger[3] showed that the unimolecular rate constant of the thermal process falls off at low pressures, due to lack of activating collisions and Sickman and Rice[4] measured the collisional activating efficiency of various inert gases. Forbes, Heidt and Sickman,[5] studying the photochemical decomposition, believed that they had discovered a lowering in the quantum yield caused by collisional deactivation of the excited molecules at high pressures. This was especially noticeable at long wave lengths, which was to be expected, since the life of an excited molecule almost certainly depends in an inverse way on the energy it contains.[6] These less highly excited molecules would be expected to have long lives, during which collisional activation could occur. It was our purpose in the present work to check this result of Forbes, Heidt and Sickman, and to see whether deactivation could also be found to occur through collision with inert gas molecules.

Although determinations of the *absolute* quantum yield would not be necessary to show deactivation, lack of agreement among earlier investigators made it desirable to redetermine this quantity. Ramsperger,[7] using filters to obtain monochromatic light, found the quantum yield at 3660 Å. to be approximately 2. His energy measurements, however, involved large corrections for red and infrared light. Forbes, Heidt and Sickman[5] reported a value for the quantum yield that approaches unity as a maximum at low pressures. These authors used the increase in the total pressure as a measure of the amount of azomethane which had reacted.

Careful analyses[8,9,10] of the products of the photodecomposition prove the reaction to be much more complicated than was originally believed and throw doubt on quantum yield determinations depending solely upon the pressure increase during reaction, since such calculations assume either an over-all decomposition giving nitrogen and ethane, or a pressure increase that is proportional to the extent of decomposition. However, other quantum yield determinations by

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[2] For references see Taylor and Jahn. *J. Chem. Phys.*, **7**, 470 (1939).

[3] Ramsperger, THIS JOURNAL, **49**, 1495 (1927).

[4] Sickman and Rice, *J. Chem. Phys.*, **4**, 239, 242, 608 (1936).

[5] Forbes, Heidt and Sickman, THIS JOURNAL, **57**, 1935 (1935).

[6] For a detailed theory see Rice and Ramsperger, *ibid.*, **49**, 1617 (1927).

[7] Ramsperger, *ibid.*, **50**, 123 (1928).

[8] Burton, Davis and Taylor, *ibid.*, **59**, 1038 (1937).

[9] Burton, Davis and Taylor, *ibid.*, **59**, 1989 (1937).

[10] Davis, Jahn and Burton, *ibid.*, **60**, 10 (1938).

Küchler[11] and by Blacet and Taurog[12] based upon the safer method of determining the nitrogen produced, are also in disagreement. Küchler found for 3131 Å. a quantum yield of approximately 2, while Blacet and Taurog's results (for 3660 Å.) agree more closely with those of Forbes, Heidt and Sickman.

We believe, on grounds which we will discuss later, that the appearance of a molecule of nitrogen means that a molecule of azomethane has decomposed, provided the reaction is interrupted before more than a few per cent. of the azomethane has been decomposed. Accordingly, we have carried out a series of determinations of the quantum yield of the photodecomposition at a number of pressures of azomethane and with azomethane–carbon dioxide mixtures by a method which consists essentially of measuring the nitrogen produced. The 3660 Å. line was used, as it has the longest wave length of any line of the mercury arc spectrum for which azomethane has considerable absorption. We may anticipate by remarking at this point that the result of these experiments was a quantum yield which we believe to be unity within the limits of error, under all conditions used. Some runs in which the change in the total pressure was followed indicate that the apparent collisional deactivation which Forbes, Heidt and Sickman[5] believed they had found resulted, in all probability, from using the total pressure change as a measure of the extent of the reaction.

Experimental Part

Azomethane was prepared by heating the addition compound of cupric chloride and dimethylhydrazine dihydrochloride according to the procedure developed by Jahn.[13] The azomethane was purified by fractionation between a dry-ice–acetone trap and a liquid air trap, after having been previously dried by calcium chloride and soda lime. The gas was stored in a 2-liter flask which was carefully shielded from light. A vapor density determination of a typical preparation gave a molecular weight of 58.5. Vapor pressure measurements on this and other preparations gave a boiling point of 0° at atmospheric pressure, in close agreement with the results of Taylor and Jahn.[2]

The azomethane was illuminated in a reaction cell with fused quartz faces. These were cemented to a piece of Pyrex tubing 8.40 cm. long and about 2.5 cm. in bore by means of de Khotinsky cement, which was itself not exposed to the direct beam of the ultraviolet light, and which was apparently not acted upon by the azomethane. The reaction cell was provided with a jacket for circulation of water at constant temperature. This was used only when changes in the total pressure were measured. The volume of the cell and connecting tubing was known, this being necessary to calculate the number of moles of gas contained therein at measured temperature and pressure.

As noted above, the reaction was followed in most of our experiments by measuring the amount of nitrogen formed. Except for small quantities of methane (of the order of 5% according to Burton, Davis and Taylor) nitrogen is the only gas in the products which will not freeze out in liquid air. The small amount of nitrogen absorbed on the frozen gases would tend to offset the small error which would be involved in not removing the small amount of methane. Consequently, an oil manometer was connected to the reaction system through a stopcock which was kept closed except when the manometer was being used. The oil used was redistilled kerosene, the fraction boiling below about 210° being discarded. After each run the gases were circulated through a liquid air trap by means of a Toepler pump, and the residual gas pressure, essentially nitrogen, was measured. The total pressure was measured before the run on a mercury manometer, and the room temperature noted, so that the concentration of azomethane in the reaction cell could be obtained.

For the runs in which the change in the total pressure was followed, a Huygens manometer, having about ten times the sensitivity of a mercury manometer, was used. The entire manometer, with the exception of the capillary arm, was placed in a thermostat that was held constant to 0.1°. Water from this thermostat was circulated through the jacket surrounding the reaction cell. Connecting tubing, however, which was not thermostated, contributed approximately 19% of the total volume of the reaction cell. The effect of a small change in room temperature on the total pressure was considered and found to be within the experimental error of these particular measurements.

The source of illumination was the constricted mercury arc of the type developed by Daniels and Heidt.[14] It was used at 100–150 volts d. c. The 3660 Å. line was isolated by means of a monochromator with large optical parts which will be described elsewhere. Monochromatic intensities behind the exit slit ranged from 9.86×10^{16} to 3.65×10^{17} photons per minute.

Light intensity was measured by a high sensitivity, low resistance d'Arsonval type galvanometer connected to a thermopile permanently placed behind the reaction cell. The thermopile was calibrated in its fixed position by means of a uranyl oxalate actinometer placed in front of the evacuated reaction cell. The actinometer solution was 0.01 *M* in uranyl oxalate and 0.05 *M* in oxalic acid.[15] The actinometer cell was 1.70 cm. deep, with faces of fused quartz 3 cm. in diameter and 1 mm. thick. The solution was continuously stirred in the dark region above the cell during irradiation.

Because of the number of faces involved, especially in the calibration of the thermopile, first-order reflections became quite significant. Reflections at the interfaces of

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[11] Küchler, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse.* Fachgruppe III (N. F.) **1**, 215 (1937).

[12] Blacet and Taurog, THIS JOURNAL, **61**, 3024 (1939).

[13] Jahn, *ibid.*, **59**, 1761 (1937).

[14] Daniels and Heidt, *ibid.*, **54**, 2381 (1932).

[15] Forbes and Heidt, *ibid.*, **56**, 2363 (1934).

the quartz and actinometer solution and secondary reflections were considered negligible. Fresnel's formula for the reflection of perpendicular light gives a value of 3.7% for the quartz–air interface at 3660 Å. If I_0 is the intensity of light entering the actinometer solution, it may be easily shown that the intensity of light registering on the thermopile junctions is given by the expression, $I_t = I_0\theta(1 - \alpha)^7$, where θ is the fraction of light transmitted by the actinometer solution, α is 0.037, and 7 is the number of faces from which reflections must be considered, including the faces of the window on the thermopile. Using the absorption coefficient of the uranyl ion as determined by Leighton and Forbes,[16] θ is found to be 0.481, and the above expression becomes $I_t = 0.366\ I_0$. In considering the reflected light entering the actinometer solution, a slight uncertainty was introduced by the fact that the reaction cell windows were not absolutely perpendicular to the beam. Careful examination led us to the approximation that half of the light reflected from the rear window of the reaction cell and from the window of the thermopile did not enter the actinometer cell. This leads to the conclusion that the total light entering the actinometer cell is given by the expression $I_c = I_0(1 + 0.169\theta)$; after introducing the value of θ, we find $I_c = 1\ 081 I_0$. Finally, then, the light absorbed by the actinometer is $I_{\text{abs.}} = (1 - \theta)I_c = 0.563 I_0 = 1.53 I_t$. The error caused by the assumption concerning the amount of reflected light entering the actinometer cell cannot produce an error of more than 2% in the quantum yield.

The calculation of the light absorbed during irradiation of the azomethane was made in a similar manner, except that here it was estimated that all of the light reflected from the rear window and three-fourths from the thermopile window passed through the reaction cell. In this case the final expression obtained is, $I'_{\text{abs.}} = 1.16(1 + 0.123\theta')(1 - \theta')I'_t/\theta'$, where the symbols have the same meaning as above, the primes indicating azomethane instead of uranyl oxalate. θ' is calculated from the cell length of 8.40 cm., the concentration of azomethane, and its absorption coefficient at 3660 Å., which we found to be 2.94, in good agreement with Ramsperger, who found 3.10.

A summary of the data involved in the calibration of the thermopile is given in Table I. The columns are, respectively, grams of uranyl oxalate solution in the cell, normality of this solution after radiation (obtained by titration with 0.08140 N potassium permanganate solution from a weight buret), number of photons absorbed using quantum yield[16] 0.49, temperature, in degrees C., time of radiation in min., average deflection in cm. of galvanometer on scale 1 meter distant, number of photons registering upon the thermopile per minute per cm. deflection of galvanometer.

TABLE I

$UO_2C_2O_4$, g.	Normality	Photons abs. $\times 10^{-18}$	Temp., °C.	Time, min.	Defl.	Calibr. const. $\times 10^{-15}$
19.3175	0.11901	0		0		
19.5123	.11872	0		0		
	Av. 0.11886					
19.6558	.11557	19.6	27	173	45.5	3.31
19.6995	.11622	15.8	27	173	42.6	2.86
19.8478	.11601	17.1	28	196	38.5	3.02
						Av. 3.06

The possible magnitude of accidental errors introduced in the calibration may be inferred from Table I, and the magnitude of such errors in the runs themselves will be seen from Table II. There are certain systematic errors introduced by having the thermopile placed behind the reaction cell instead of in front of it. Some of these have to do with the calculation of the amount of reflection. We have already estimated these to be of the order of 2% (assuming, of course, that the actual reflection coefficient of our windows is given closely by the tabulated data on fused quartz). The estimated error from this source is this low because the errors for the calibration and for the actual runs will, at least, in part, be in the same direction.

Other systematic errors, which are increased by placing the thermopile behind rather than in front of the cell, are connected with possible errors in the absorption coefficients of the materials. The reason for this is that the number of photons absorbed is proportional to $(1 - \theta)I_0$. When I_0 is not measured, but rather I, the transmitted intensity, the number of photons absorbed is proportional to $[(1 - \theta)/\theta]I$. An error due to θ is thus magnified, as θ comes in twice. In the case of the actinometer solution, θ may be in slight error, since we used Leighton and Forbes' values for 25°, whereas our temperatures were as much as 3° higher. On the basis of the temperature coefficient for the absorption coefficient of a uranyl oxalate solution given by Leighton and Forbes, we estimate that our calibration (galvanometer deflection per quantum) may be 4 or 5% low, and our quantum yield for azomethane also this much too low.

On the other hand, the absorption coefficient of azomethane obtained by Ramsperger (3.10) differs from ours (2.94) in such a direction that if we were in error in using our own, it makes our quantum yield too high, the percentage errors being 6 and 12% at 10 and 60 cm., respectively. Since these possible errors are in opposite directions, we have decided to attempt no correction. The calculations will indicate the possible order of magnitude of errors due to absorption coefficients.

The effect of putting the thermopile back of the absorption cell is well brought out by considering what effect the change from an absorption coefficient of 2.94 to one of 3.10 would produce if the thermopile were used in the usual manner in front of the cell. The errors then would be 5 and 2%, instead of 6 and 12%. The disadvantage apparent in placing the thermopile behind the cell is, we believe, compensated for by the added convenience and the fact that there is no doubt that the thermopile is always in the same position relative to the cell and the light beam.

Results

Table II shows all data and results obtained in the series of runs on azomethane alone at various pressures. In order, the columns are: pressure of azomethane in cm., temperature, time of irradiation in min., number of photons incident per

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[16] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930); see also ref. 15.

min., total number of photons absorbed, number of molecules decomposed, quantum yield. The results show that the quantum yield of the decomposition is unity to within 12–15%, when calculated on the assumption that the appearance of a nitrogen molecule means the disappearance of an azomethane molecule.

The runs are given in the order in which they were done. The reaction cell was filled with fresh azomethane except for the runs at 39.1, 43.9 and 23.2 cm., where more azomethane was added after the residual nitrogen was pumped off. No deactivation, within experimental error, is apparent for pressures up to 63 cm.

TABLE II

P_{azo}, cm.	Temp., °K.	Time, min.	I_0 × 10^{-16}	Ph. abs. × 10^{-18}	Moles dec. × 10^{-18}	ϕ
6.63	300	57.5	13.4	1.41	1.25	0.89
39.1	300	38.0	13.5	3.55	3.13	.88
8.90	299	60.0	17.3	2.48	1.71	.69
43.9	298	40.0	14.3	4.23	3.47	.82
23.4	302	38.0	22.8	4.40	3.71	.84
23.2	300	43.0	23.8	5.20	4.46	.86
63.0	301	30.0	16.3	4.18	3.86	.92
19.9	306	40.0	18.3	3.28	3.36	1.02
19.9	306	40.0	15.0	2.70	2.85	1.06
10.3	306	37.5	24.2	2.39	2.56	1.07
39.0	306	32.5	19.0	4.23	4.70	1.11

Although there seems to be a trend toward larger quantum yields during the course of the experiments, such a trend would not mask deactivation effects if they were present, since the pressures were chosen quite at random. A possible explanation of such a trend would be the formation of a deposit upon the reaction cell windows, since the thermopile was placed *behind* the reaction cell, and the light absorbed was calculated from the absorption coefficient. Moreover, the effect would be cumulative because it was not practicable to clean the cell after each run. There was no visual evidence of such a deposit, although the small extent of decomposition may be responsible for its not having been observed. That some condensation takes place is plausible, for at shorter wave lengths a deposit is quite noticeable,[5,8] and at high temperatures a condensed liquid actually has been observed.[9] The correction of the thermopile calibration for such a deposit would be complicated by the fact that the actinometer cell was placed in front of the reaction cell, so that light passing through the actinometer would have to go through a deposit on the front, as well as the rear, window, before reaching the thermopile. However, since the calibration was made fairly early in the set of runs (between the fourth and fifth) it seems unlikely that this would affect the calculated quantum yield very greatly.

Table III shows runs made with practically constant azomethane pressure, but widely varying pressures of carbon dioxide. The columns are the same as those in Table II. Fresh azomethane was used for each group of runs. After each run the residual nitrogen pressure was measured, the nitrogen pumped off, and carbon dioxide added as desired for the next run. As is to be expected on the basis of Table II, carbon dioxide shows no ability to deactivate the excited azomethane molecule even when present in the ratio of 11 to 1 at 70 cm. total pressure. The average quantum yield for pure azomethane agrees with that in Table II within the limits of error. In general, the agreement within a group is rather better than the agreement from group to group. It should be pointed out that these runs preceded those given in Table II, and that the reaction cell was cleaned and realigned before the data in Table II and the thermopile calibration were made. However, failure to exactly duplicate the alignment of cell and thermopile cannot cause an error of more than a few per cent. in the results.

TABLE III

P_{azo}, cm.	P_{CO_2}, cm.	Temp., °K.	Time, min.	I_0 × 10^{-16}	Ph. abs. × 10^{-18}	Moles dec. × 10^{-18}	ϕ
5.54	0	306	103	16.8	2.62	2.06	0.79
5.44	0	306	103	12.5	1.91	1.58	.83
5.36	0	306	103	12.6	1.93	1.66	.86
5.28	10.07	306	103	11.4	1.72	1.85	1.07
5.54	0	306	103	9.86	1.55	1.33	0.85
5.43	0	306	103	10.6	1.63	1.41	.87
5.36	9.34	306	117.5	10.2	1.77	1.50	.85
5.28	9.34	306	103	10.4	1.57	1.38	.88
5.21	24.14	304	117.5	13.9	2.40	1.92	.80
5.12	24.14	303	117.5	17.2	2.44	1.91	.78
5.02	24.14	303	117.5	15.3	2.55	2.15	.84
5.48	0	303	117.5	13.5	2.24	2.12	.95
5.37	0	303	103	12.8	1.98	1.63	.82
5.47	0	300	58.7	26.3	2.36	1.74	.74
5.38	0	300	38.7	35.2	2.05	1.56	.76
5.30	64.05	300	38.7	36.5	2.10	1.61	.77
5.21	64.05	300	38.7	36.2	2.05	1.55	.76
5.85	0	301	60.0	30.6	2.99	2.22	.74
5.73	68.35	301	60.0	30.6	2.93	2.20	.75

It may be remarked that the results in Tables II and III indicate that the quantum yield is independent of light intensity over an almost fourfold range, at least at low azomethane pressures.

Table IV includes data obtained by measuring the pressure increase during the photolysis. ΔP_H is the increase in mm., as measured by the slope of the best line through a pressure *vs.* time plot multiplied by the time of the run, I_0 is the incident light intensity in arbitrary units, Ph. abs. is the total light absorbed, also in arbitrary units, and ϕ' is the relative quantum yield obtained by arbitrarily making the quantum yield unity at 10 cm. pressure. Each group of runs must be considered independently, for the arbitrary units for I_0 are not comparable from group to group. However, necessary reflection corrections have been made, since these depend on the pressure. Although the experimental error in these results was somewhat greater than that in Tables II and III, the relative quantum yields show conclusively that the increase in total pressure of azomethane for a given absorption of light is progressively less as the azomethane pressure is increased. These results definitely indicate that ϕ cannot be measured by measuring the pressure increase, as has been assumed by a number of previous investigators. Since all the investigations of the thermal decomposition have used the total pressure increase as the measure of the amount of reaction, they may be in error, too, though this is not necessarily true, since the conditions of the experiments were very different, and the internal evidence points to their reliability.

TABLE IV

P_{azo}, cm.	Time, min.	ΔP_H, mm.	I_0	Ph. abs.	ϕ'
10.0	70	1.26	2.33	4.20	1.00
19.9	60	1.39	2.07	5.49	0.85
19.9	60	1.06	1.85	4.96	.71
35.9	120	1.68	3.41	26.9	.37
19.3	60	1.24	3.34	8.76	.86
9.7	95	1.31	3.28	7.87	1.00
42.3	150	2.72	3.14	33.8	0.43
32.7	60	1.30	3.00	11.2	.61
10.1	90	1.46	3.31	7.73	1.00
19.9	40.0	1.14	5.15	9.22	0.72
19.9	40.0	0.84	4.23	7.57	.65
10.3	37.5	1.16	6.85	6.75	1.00
39.0	32.5	0.90	5.33	11.9	0.44

A few runs were made in which carbon dioxide was added to 5 cm. of azomethane and the decomposition followed by measuring the total pressure change. These results were very uncertain, but appeared to indicate that carbon dioxide had no effect on the rate of pressure increase, within about ±25%.

Discussion

If the data in Table IV are compared with those in Tables II and III, it appears obvious, in agreement with Burton, Davis and Taylor,[8,9,10] that azomethane may react by other processes than by simple decomposition into nitrogen and alkanes. The mechanism of such a process is, however, open to speculation. Burton, Davis and Taylor have supposed, in common with many others, that the primary decomposition is into nitrogen and methyl radicals, and have suggested that addition of methyl to azomethane may take place. If this addition product is stable, or becomes stable through a rearrangement or reaction, under the conditions of the experiment, such a hypothesis may explain the results, because any methyl radical which adds to an azomethane molecule does not contribute to the increase in pressure. It would be necessary, however, if this hypothesis is to explain these results, that the probability be extremely small that a single collision of a methyl radical with an azomethane molecule should result in such an addition, so that at low azomethane pressures most of the radicals would be removed at the walls. Such a mechanism would mean that the ethane formed in the photolysis (about 42% of the gaseous reaction products at low pressures[8]) should decrease with rising pressure. Unfortunately, Burton, Davis and Taylor did not use pressures above 10 cm. for their studies. The last four runs in Tables II and IV, of the present paper, are the same, both types of measurements having been made simultaneously. They are compared in Table V, where ΔP_H is the pressure increase during the reaction in mm., and P_r is the pressure of nitrogen formed in mm. On the basis of this hypothesis, the ratio in the last column should represent roughly the extent to which ethane is formed at the walls.[17]

The justification of the use of the nitrogen pressure to measure the quantum yield must be closely connected with the results just discussed. Any

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[17] It has been remarked that addition of a certain pressure of carbon dioxide on the quantum yield, as calculated from total pressure increase, has much less effect than a similar addition of azomethane. This is readily understood if we remember that carbon dioxide can only delay the passage of methyl radicals to the walls, but not remove them. This does mean that a methyl will have more collisions with azomethane molecules on the way to the walls, and so should have a somewhat greater chance of being removed. But the addition of more azomethane is much more effective, for the collisions with the extra azomethane are not only delaying, but may themselves result in removal of the methyl radical.

TABLE V

P_{azo}	ΔP_H	P_r	$\Delta P_H/P_r$
19.9	1.14	1.69	0.68
19.9	0.84	1.44	.58
10.3	1.16	1.29	.90
39.0	0.90	2.36	.38

nitrogen which appears must be produced in one of two ways: either it comes from the direct decomposition of azomethane, or it comes from the decomposition of the addition products just mentioned. Unless these products are considerably less stable than azomethane, the production of nitrogen must, in general, come from the direct decomposition of azomethane when the percentage of decomposition is as small as it is in the experiments we have performed, for under these conditions the azomethane is always present in great excess. If the addition product were sufficiently unstable so that an appreciable amount of the nitrogen was produced by it, we should expect two results. In the first place, the fragmentation of the addition product would mean that it would contribute to the pressure, and the last column of Table V should be more nearly constant. The variation in this column indicates, in itself, that the nitrogen production is not closely related to the secondary products present. In the second place, the fragments from the addition product would be expected to react with more azomethane, producing more addition product, which would again decompose, thus setting up a chain. But Davis, Jahn and Burton[10] have shown that there is no chain by finding no inhibiting effect of nitric oxide on the production of nitrogen, and the entire behavior of azomethane is best explained on the assumption that no chain is involved. The very fact that nitric oxide has no effect on the nitrogen production is itself evidence that nitrogen is a measure of the amount of azomethane decomposed, for the nitric oxide presumably removes the methyl radicals without allowing formation of the addition compound.

It is unfortunate that there are no analyses of azomethane decomposed at higher pressures than about 10 cm., in order to check the possibility that the non-condensable gas contains appreciable quantities of methane at the higher pressures. This seems unlikely, however, since the methyl radical appears, at the higher pressures, to enter predominantly into reactions which decrease the pressure.

We wish to thank our technician, Mr. A. R. Bennett, for his skillful assistance in the construction of the monochromator, and the Smith Bequest of the University of North Carolina for a grant toward the cost of the instrument. We also wish to thank Professor Alfred Russell and the organic preparations class for the dimethylhydrazine hydrochloride from which the azomethane was made, and Professor Edward Mack, Jr., for the thermopile used throughout these experiments.

Summary

1. The photodecomposition of azomethane has been studied and it has been found that the quantum yield at 3660 A. is unity within the limits of experimental error. It remains unity up to a pressure of 63 cm., showing no indication of the occurrence of deactivation by collision.

2. The quantum yield is unaffected by a fourfold variation of light intensity.

3. The quantum yield is unaffected by a considerable excess of carbon dioxide.

4. The increase in total pressure does not give a measure of the amount of decomposition. The ratio of the total pressure increase to the nitrogen produced decreases with pressure; possible reasons for this effect have been discussed in terms of secondary reactions.

CHAPEL HILL, N. C. RECEIVED MAY 26, 1941