Studies of the Cage Effect of Solvent. I. Photolysis of Azomethane in n-Hexane

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The concept of the cage effect of solvent molecules given in 1936 by Frank, Rabinowitch and Wood[1] has since then frequently been used to explain such experimental findings as the low quantum yield in a photochemical reaction in solution. The presence of the cage effect has been reported in a number of thermal, photochemical or radiation-induced decomposition reactions of the following substances: iodine[2], acetyl peroxide[3], butyryl peroxide[4], α, α'-azobisisobutyronitrile[5], halides[6], etc. To date, however, reliable quantitative studies of the cage effect have been meagre.

It has been found by the present author that the photolysis of azomethane in solution

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[1] J. Frank and E. Rabinowitch, *Trans. Faraday Soc.*, **32**, 138 (1936); E. Rabinowitch and W. C. Wood, ibid., **32**, 547 (1936).

[2] R. M. Noyes et al., *J. Chem. Phys.*, **18**, 658, 999 (1950); *J. Am. Chem. Soc.*, **76**, 2140 (1954); R. L. Strong and J. E. Willard, ibid., **79**, 2098 (1957).

[3] M. Szwarc et al., ibid., **76**, 5981 (1954); ibid., **77**, 3486 (1955); *J. Chem. Phys.*, **23**, 1978 (1955); J. R. Nash, W. H. Hamill and R. R. Williams, *J. Phys. Chem.*, **60**, 823 (1956).

[4] J. Smid, A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3315 (1956).

[5] G. S. Hammond et al., ibid., **77**, 3244 (1955); ibid., **81**, 4878 (1959); ibid., **82**, 5394 (1960); J. C. Roy, J. R. Nash, R. R. Williams and W. H. Hamill, ibid., **78**, 519 (1956); C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56**, 815 (1960).

[6] J. E. Willard, *J. Am. Chem. Soc.*, **73**, 2271 (1951); ibid., **74**, 318 (1952); M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952); J. C. Roy, W. H. Hamill and R. R. Williams, *J. Am. Chem. Soc.*, **77**, 2593 (1955).

exhibits a large cage effect; photolysis has therefore been investigated in various solvents. This paper reports on the study in *n*-hexane solution. The results obtained in other solvents will be reported in a later paper.

Experimental

Materials. — Azomethane was prepared by the thermal decomposition[7] of azomethane-cuprous chloride[8] produced from dimethyl hydrazine dihydrochloride[9], purified by removing water and carbon dioxide with calcium chloride and soda lime respectively and by several-times-repeated distillation from a dry ice-acetone trap to a liquid nitrogen trap in vacuo, and stored in a reservoir protected from light. *n*-Hexane was purified as follows: the commercial hexane of a chemically pure grade was repeatedly washed with chlorosulfonic acid for about a month, stirred with alkaline and acid potasium permanganate solutions, washed with sodium carbonate and water, dried over phosphorus pentoxide, and distilled; the fraction 68 to 69°C was then collected. The hexane thus purified showed no absorption in the wavelength range above 250 mμ. Styrene was used as a scavenger of methyl radicals because of its large methyl affinity[10]. It was also purified by vacuum distillation.

Apparatus.—The photolysis was carried out with 366 and 313 mμ obtained from an ultra-high pressure mercury lamp of 100 Watt (Mazda, SHL-100UV). The filter used for 366 mμ was UV-D1 (Mazda). The transmission ratios of 334 and 390 mμ to 366 mμ were about 6 and 1% respectively. For 313 mμ a 1.8 M solution of nickel sulfate 1 cm. in thickness was used, with a glass plate to cut off the light of shorter wavelengths than 290 mμ. The transmission ratios of 334 and 300 mμ to 313 mμ were roughly 29 and 22% respectively.

The reaction cell used for the photolysis below room temperature was a glass cylinder 3.6 cm. in diameter and 1.0 cm. in length, with a capacity of 10 ml. It was connected to the other parts of the apparatus by a mercury cut-off. For the experiments above room temperature, a cell of the same size but with two side tubes was used. One of these side tubes was made of capillary tubing, and was sealed off after the introduction of the reactants, and the other had a breakable seal for analysis of the products. All the side tubes were made of brown-colored glass to prevent the decomposition of azomethane vapor in those parts. A non-plated Dewar vessel was used as a bath in the experiments with 366 mμ, but for those with 313 mμ a copper-made bath equipped with a quartz window was used.

The Procedure.—Before use hexane was subjected to thrice-repeated bulb-to-bulb distillation using dry ice-acetone and was introduced into the reaction cell. When styrene was used as a scavenger, it was introduced into the cell in a similar way. Azomethane was also purified each time before use by condensation and evacuation at −160°C; it was then introduced into the reaction cell cooled with liquid nitrogen. After closing the mercury cut-off or sealing off the capillary tubing, the cell was warmed to room temperature to get a complete mixing of azomethane with hexane. The cell was then immersed in the bath at the experimental temperature and the photolysis started. The mercury cut-off was used also as a manometer, to measure both pressures of hexane and azomethane and the increase in pressure due to the photolysis.

The reaction cell was cooled with dry ice-acetone after the irradiation was over, and it was connected to the analytical system by the mercury cut-off or by the breakable seal. The cell contained hexane, undecomposed azomethane, nitrogen, methane, ethane, various by-products, and styrene if used. The gaseous components were separated by twice-repeated bulb-to-bulb distillation at the dry ice-acetone temperature and cooled to −160°C to condense azomethane, hexane vapor and by-products. Ethane was then condensed at the liquid nitrogen temperature. Nitrogen and methane that were not condensed were collected in a Toepler gauge, and the sum of their amounts were determined. The mixture was then sent into a platinum combustion tube, where the methane was burnt to carbon dioxide and water. By removing the water by condensation, the amount of carbon dioxide was determined; this gave in turn the amount of methane and, accordingly, that of nitrogen. Ethane condensed in the liquid nitrogen trap was evaporated, collected in the Toepler gauge, and its quantity determined.

Results

Table I shows the results obtained at 0°C. *V* is the volume of the solution at the reaction temperature. CH_4/N_2 and C_2H_6/N_2 represent respectively the yields of methane and ethane referred to nitrogen. The material balance for nitrogen, methane and ethane is represented by $((1/2)CH_4+C_2H_6)/N_2$, since two

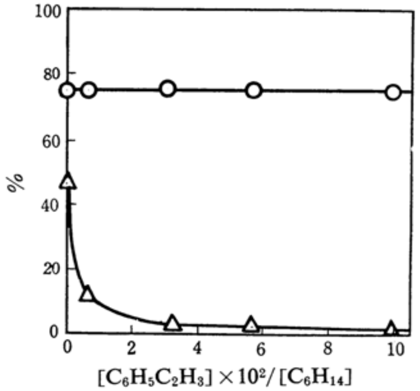

Fig. 1. Effect of styrene on yields of methane and ethane at 0°C.
○, C_2H_6/N_2; △, CH_4/N_2

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[7] F. P. Jahn, ibid., **59**, 1761 (1937).

[8] O. Diels and W. Koll, *Ann.*, **443**, 262 (1925).

[9] H. H. Hatt, "Organic Syntheses", Vol. XVI (1936), p. 18.

[10] F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *J. Am. Chem. Soc.*, **77**, 5493 (1955); M. Feld and M. Szwarc, ibid., **82**, 3791 (1960).

TABLE I. PHOTOLYSIS OF AZOMETHANE IN *n*-HEXANE AT 0°C

Run No.	Wave-length mμ	V cc.	$[(CH_3)_2N_2]\times 10^2$ mol./l.	$\frac{[C_6H_5C_2H_3]}{[C_6H_{14}]}$ %	Time of irradiation min.	Rate of formation $\times 10^{11}$ mol. cc^{-1} sec^{-1}			$\frac{CH_4}{N_2}$ %	$\frac{C_2H_6}{N_2}$ %	$\frac{\frac{1}{2}CH_4+C_2H_6}{N_2}$ %
						R_{N_2}	R_{CH_4}	$R_{C_2H_6}$			
1[a]	366	13.4	0.852	0	90	11.7	0.448	11.0	3.83	94.1	96.0
2[a]	366	13.4	0.993	0	90	13.8	0.607	12.7	4.40	91.8	94.0
3	366	13.4	0.826	0	198	7.40	3.48	5.57	47.0	75.3	98.8
4	366	13.4	0.898	0	162	7.85	3.64	5.94	46.4	75.7	98.9
5	366	11.2	1.13	0	84	15.5	7.35	11.6	47.5	75.2	99.0
6	366	11.2	1.17	0	66	21.8	10.3	16.4	47.4	75.0	98.7
7	366	10.5	3.23	0	60	49.6	23.2	37.4	46.7	75.5	98.9
8	366	9.9	3.30	0	60	37.1	17.0	28.0	45.8	75.8	98.3
9	366	11.2	4.20	0	48	30.6	14.2	23.1	46.3	75.5	98.6
10	313	10.8	2.70	0	90	13.3	6.25	10.0	47.0	75.4	98.9
11	313	10.6	2.78	0	90	19.0	9.04	14.3	47.6	75.2	99.0
12	>300	9.9	3.50	0	24	108.0	50.3	81.5	46.6	75.4	98.7
13	366	11.3	4.12	0.612	54	32.7	3.80	24.5	11.6	74.9	
14	366	11.1	3.06	3.16	42	45.6	1.37	34.5	3.0	75.7	
15	366	10.6	2.80	5.65	42	43.3	1.08	32.5	2.5	75.2	
16	366	12.5	3.55	9.92	60	28.3	0.44	21.2	1.6	75.0	

a) Runs 1 and 2 are the results obtained with azomethane vapor.

TABLE II. PHOTOLYSIS OF AZOMETHANE IN *n*-HEXANE AT VARIOUS TEMPERATURES

Run No.	Temp. °C	V cc.	$\frac{[C_6H_5C_2H_3]}{[C_6H_{14}]}$ %	Time of irradiation min.	Rate of formation $\times 10^{11}$ mol. cc^{-1} sec^{-1}			$\frac{CH_4}{N_2}$ %	$\frac{C_2H_6}{N_2}$ %	$\frac{\frac{1}{2}CH_4+C_2H_6}{N_2}$ %
					R_{N_2}	R_{CH_4}	$R_{C_2H_6}$			
17	80	12.2	0	48	22.0	16.3	13.2	74.0	60.0	97.0
18	75	11.3	3.48	60	39.4	5.36	24.1	13.6	61.2	
19	50	11.3	0	42	34.1	22.5	21.8	63.8	65.9	97.8
20	50	10.9	3.47	72	40.2	3.54	26.3	8.81	66.0	
21	25	10.5	3.47	72	36.0	1.90	25.8	5.29	71.6	
22	20	10.8	0	54	31.6	22.9	17.0	53.8	72.6	99.5
23	−31	9.5	0	60	38.6	13.8	31.2	35.8	80.9	98.8
24	−31	10.6	3.18	42	38.2	0.69	30.6	1.80	80.2	
25	−50	11.3	0	60	29.6	9.24	24.8	31.2	83.9	99.5
26	−50	10.3	3.18	42	32.7	0.46	27.3	1.43	83.5	
27	−75	10.3	0	240	4.82	1.02	4.27	21.2	88.7	99.3
28	−75	9.0	0	42	32.0	6.72	28.3	21.0	88.5	99.0
29	−75	10.3	0	90	35.4	7.72	31.3	21.8	88.3	99.2
30	−75	10.2	0.607	120	21.5	0.71	18.5	3.30	86.3	
31	−75	9.9	3.20	42	26.8	0.30	23.4	1.14	87.5	
32	−75	10.5	10.7	72	10.4	0.13	8.99	1.26	86.8	

methyl radicals and a nitrogen molecule are obtained from an azomethane molecule. The extent of conversion was less than 6% in all the runs except in Runs 3 and 4, where it was nearly 10%.

Runs 1 and 2 show the results of the photolysis of azomethane vapor carried out in comparison with those in solution. Figure 1 shows the variation in yields of methane and ethane with the concentration of styrene in the series of Runs 13−16.

Table II shows the effect of temperature on the photolysis with 366 mμ. The concentration of azomethane in each run was about 3×10^{-2} mol./l. The conversion in each run was again less than 6%. Figure 2 summarizes the results given in Tables I and II, $(CH_4/N_2)_s$ and $(C_2H_6/N_2)_s$ denoting respectively the yields of methane and ethane in the presence of styrene of 3.16 to 3.48 mol. %.

Figure 3 shows the effect of temperature on the quantum yield of photolysis determined as follows: Runs 1—4 show that the ratio of the quantum yield in solution against that in

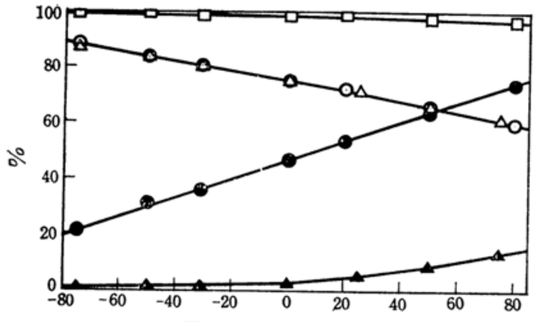

Fig. 2. Effect of temperature on yields of methane and ethane, and material balance.
□, $((1/2)CH_4+C_2H_6)/N_2$
○, C_2H_6/N_2; △, $(C_2H_6/N_2)_s$
●, CH_4/N_2; ▲, $(CH_4/N_2)_s$

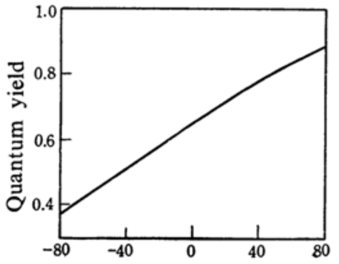

Fig. 3. Dependence of quantum yield on temperature.

the vapor phase is 0.65; since in the vapor phase the quantum yield is reported to be unity[11], those in solution at various temperatures are obtained by comparing rates of the formation of nitrogen. However, in view of various uncertainties involved, the quantum yields thus determined have to be taken only as apparent values.

Discussion

The photolysis of azomethane has been studied in the gas phase by a number of workers[11,12] The mechanism that accounts for the main products, i. e., methane, ethane and nitrogen, is relatively simple and can be represented as

$$(CH_3)_2N_2+h\nu \rightarrow 2CH_3+N_2$$
$$CH_3+(CH_3)_2N_2 \rightarrow CH_4+CH_3N_2CH_2$$
$$CH_3+CH_3 \rightarrow C_2H_6$$

The following addition reactions of methyl radicals have also been proposed to explain the fate of methyl radicals that are not accounted for by methane and ethane:

$$CH_3+(CH_3)_2N_2 \rightarrow (CH_3)_3N_2$$
$$CH_3+(CH_3)_3N_2 \rightarrow (CH_3)_4N_2$$
$$CH_3+CH_2N_2CH_3 \rightarrow C_2H_5N_2CH_3$$

The possibility of the direct formation of ethane by the primary process has been excluded by the experiments carried out with a scavenger such as nitric oxide[12a] and butadiene[12b]. The decomposition into three fragments in the primary act may actually take place in two stages, i. e.,

$$(CH_3)_2N_2+h\nu \rightarrow CH_3N_2+CH_3$$
$$\text{and } CH_3N_2 \rightarrow CH_3+N_2$$

However, since the radical CH_3N_2 is very short-lived[13], such a two-stage decomposition cannot be discriminated from that given above so far as subsequent reactions are concerned.

On the basis of the mechanism thus established in the gas phase, the possible reactions in *n*-hexane solution may be supposed as follows:

$$(CH_3)_2N_2+h\nu \rightarrow [2CH_3+N_2] \qquad (1)$$
$$[2CH_3+N_2] \rightarrow C_2H_6+N_2 \qquad (2)$$
$$\rightarrow CH_3+N_2+CH_3 \qquad (3)$$
$$[2CH_3+N_2]\,C_6H_{14} \rightarrow CH_4+C_6H_{13}+N_2+CH_3 \qquad (4)$$
$$[2CH_3+N_2]\,C_6H_5C_2H_3 \rightarrow C_6H_5C_3H_6+N_2+CH_3 \qquad (5)$$
$$CH_3+C_6H_{14} \rightarrow CH_4+C_6H_{13} \qquad (6)$$
$$CH_3+CH_3 \rightarrow C_2H_6 \qquad (7)$$
$$CH_3+(CH_3)_2N_2 \rightarrow CH_4+CH_2N_2CH_3 \qquad (8)$$
$$\rightarrow (CH_3)_3N_2 \qquad (9)$$
$$CH_3+C_6H_{13} \rightarrow C_6H_{13}CH_3 \qquad (10)$$
$$CH_3+C_6H_5C_2H_3 \rightarrow C_6H_5C_3H_6 \qquad (11)$$
$$C_6H_{13}+C_6H_{13} \rightarrow C_{12}H_{26} \qquad (12)$$
$$\rightarrow C_6H_{14}+C_6H_{12} \qquad (13)$$

The parenthesis in the primary process denotes that two methyl radicals and a nitrogen molecule are formed together in a solvent cage. Reactions 2 and 3 represent respectively the ethane formation in the solvent cage and the separation of the two methyl radicals from each other by diffusion. Reaction 4 is the hydrogen atom abstraction by one of the

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[11] M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).

[12] a) T. W. Davis, F. P. Jahn and M. Burton, *J. Am. Chem. Soc.*, **60**, 10 (1938); b) S. Kodama and O. Toyama, to be published; c) W. C. Seppy and J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959); d) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 39 (1955); e) S. Toby and K. O. Kutschke, ibid., **37**, 672 (1959); f) S. Toby, *J. Am. Chem. Soc.*, **82**, 3822 (1960).

[13] The decomposition of the CH_3N_2 radical is exothermic by some 29 kcal./mol. (Ref. 14). Sleppy and Calvert (Ref. 12) failed to detect the radical spectroscopically in a flash photolysis of azomethane.

[14] C. Steel and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1959**, 975.

methyl radicals from a solvent molecule constituting the cage, and reaction 5 is an analogue in the case where a styrene molecule participates in constituting the cage. Reactions 6—10 represent various possibilities for methyl radicals distributed at random in the solution. Reaction 11 shows the scavenger action of styrene. Reactions 12 and 13 give possible fates other than reaction 10 for hexyl radicals formed by reaction 6.

The sequence of reactions given above is only a crude picture, but the results obtained in the present work may be discussed by referring to these reactions. The reactions that explain the formation of ethane are those numbered from 2 and 7. As shown in Tables I and II and in Fig. 1, the addition of styrene in an increasing amount reduces the yield of methane nearly to zero, whereas that of ethane remains unaffected, indicating that ethane is formed exclusively by reaction 2 or by the combination of methyl radicals in the solvent cage. Even in the absence of styrene, the results obtained lead to the same conclusion: If ethane is formed by reaction 7, its rate should be proportional to the second power of the steady concentration of methyl radicals, while the rate for methane would be simply proportional to its first power, Runs 3—9, given in Table I, show, however, that the yields of methane and ethane are not affected by increasing the concentration of azomethane, i. e., by increasing the amount of azomethane decomposed per unit time.

As to the formation of methane, the most important process may be supposed to be reaction 6. The effect of styrene shown in Tables I and II and in Fig. 1 is consistent with what is expected for this reaction. Reaction 8 cannot be important, since the mole ratio of azomethane (to *n*-hexane) is (of the order) of 10^{-3} in the present work and the rate constants for reactions 6 and 8 may be of the same order of magnitude[15]. The contribution of reaction 4 is also negligible. If this reaction were important, reaction 5 should also be important; otherwise, the nearly complete suppression of methane formation by styrene could not be explained. However, if reaction 5 were important, the yield of ethane should be reduced in the presence of styrene, which contradicts what was actually found to be true.

The quantum yield of photolysis is, as has been already described, less than unity in *n*-hexane solution, and Fig. 3 shows that it decreases markedly with the lowering of the temperature. In general, a low quantum yield less than unity may be accounted for either by the deactivation of excited substrate molecules or by the recombination of the primary products in the solvent cage, provided that no substrate molecules are regenerated by secondary reactions. Studies of the yield of fluorescence in solution show, however, that quenching by deactivation usually increases with the rise in temperature[16]. The observed falling off of the quantum yield with the lowering of the temperature seems, therefore, to have resulted from the recombination of the initially formed radicals CH_3N_2 and CH_3 in the solvent cage, though the former radical is short-lived, as has been described above, and may not take part in subsequent reactions.

The decomposition of the azomethane molecule into two metyl radicals and a nitrogen molecule requires an energy of 22 kcal./mol[14]. Hence, the photolysis with 366 mμ produces an excess energy of 56 kcal./mol. Though how this excess energy is distributed among the three fragments formed is not clear, there is a possibility that hot methyl radicals are thus formed. In fact, Sleppy and Calvert[12c] concluded, in a flash photolysis of azomethane vapor, the formation of hot methyl radicals from the effect of wavelengths on the yield ratio CH_4/C_2H_6 and from the effect of the addition of C_2F_6. In ordinary photolysis of azomethane, however, no indication of their existence has been reported. Also, in this work, as is shown in Table I, the irradiation with 313 mμ gave almost the same result as that for 366 mμ, although the energy difference between the two mercury lines is not very large (13 kcal./mol.).

As is shown in Fig. 4, the dependence of the yield of ethane on the temperature is approximately represented by

$$1-C_2H_6/N_2=A\exp(-E/\boldsymbol{RT})$$

with $A=2.08$ and $E=1.17$ kcal./mol. Though the energy value found here probably has some correlation with the diffusion energy of methyl radicals in *n*-hexane, the latter quantity cannot be computed directly from such an energy value since the formula given above is merely an empirical one[17].

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[15] The rate constants in the gas phase are $k_6=10^{11.1}$ exp $(-8100/\boldsymbol{RT})$ and $k_8=10^{11.1}\exp(-7600/\boldsymbol{RT})$ mol^{-1} cc. sec^{-1}. (A. F. Trotman-Dickenson, "Gas Kinetics", Butterworths, London (1955), p. 200.)

[16] For example, E. J. Bowen and J. Sahn, "Photochemistry in the Liquid and Solid States", Ed. by F. Daniels, John Wiley and Sons, Inc., New York and London (1960), p. 55.

[17] A simple treatment of reactions 6 and 7 leads to an expression

$$C_2H_6/N_2=k_6/(k_6+k_7)$$

or

$$[1-(C_2H_6/N_2)]/(C_2H_6/N_2)=k_7/k_6$$

where k_6 and k_7 are respective rate constants. If, therefore, k_6 is assumed to be independent of temperature, the Arrhenius plot of the quantity on the left-hand side of the latter equation can be expected to yield the diffusion energy of methyl radicals. The results given in Table II, however, do not give a linear plot, indicating that such a treatment is too crude.

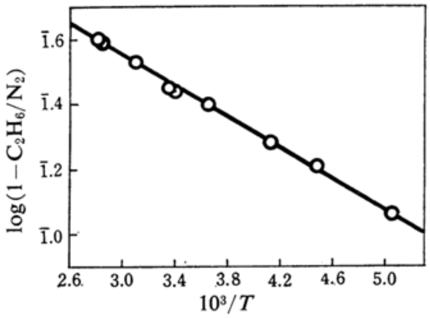

Fig. 4. Arrhenius plot of $1-C_2H_6/N_2$.

As seen in Table II and Fig. 2, the material balance referring to methane and ethane, $((1/2)CH_4+C_2H_6)/N_2$, is nearly 100% below room temperature but slightly falls off at higher temperatures. As has been proposed in the gas phase, the loss in the material balance may be ascribed to addition reactions of methyl radicals such as reactions 9 and 11.

There have been found a number of compounds similar to azomethane in that three fragments are formed by the decomposition of a substrate molecule. Some examples are acetone[18], ethyl methyl ketone[19], diethyl ketone[19], acetyl peroxide[3], butyryl peroxide[4] and dimethyl mercury[20]. None of them, however, have been reported to show such a large cage effect as has been found in the present work. The reason why azomethane behaves exceptionally probably comes from the way in which it decomposes. As has been already described, in the case of azomethane two methyl radicals and a nitrogen molecule are formed almost simultaneously, while in other cases, the decomposition of a substrate molecule probably occurs more clearly in two stages:

$$XYZ \rightarrow XY+Z$$
$$XY \rightarrow X+Y$$

If, therefore, the lifetime of the XY radical is sufficiently large[21], it will become separated from the radical Z before decomposition, and the cage combination $X+Z \rightarrow XZ$ will not be observed. It may still be expected in this case that the recombination $XY+Z \rightarrow XYZ$ takes place in the solvent cage and that this will result in a lowering of the quantum yield, as has been found in the present work. However, such a cage recombination cannot be estimated from quantum yields unless the deactivation of excited substrate molecules is proven to be absent.

Summary

Azomethane in *n*-hexane solution has been decomposed by irradiation of 366 mμ over the temperature range −75 to 80°C, in order to study the effect of the solvent cage on the photolysis. The main products have been found to be nitrogen, methane and ethane. The yield of methane increases, but that of ethane, which amounts to 88% of nitrogen at −75°C, decreases with the rise in temperature. The addition of styrene as a scavenger for methyl radicals in an increasing amount suppresses the formation of methane almost completely, while that of ethane is not affected, indicating that ethane is exclusively formed by the cage combination of an azomethane molecule. The formation of methane is explained by the abstraction of the hydrogen atom from a solvent molecule by methyl radicals that have escaped the original cage. The material balance represented as $((1/2)CH_4+C_2H_6)/N_2$ is nearly 100% below room temperature, but it falls off slightly at higher temperatures; this may be ascribed to addition reactions of methyl radicals. The quantum yield of photolysis is apparently smaller than unity and falls off with a lowering of the temperature; this probably arises from the cage recombination of the initially formed pair of radicals CH_3N_2 and CH_3, though the former radical is very short-lived.

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[18] R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955); D. B. Peterson and C. J. Mains, *J. Am. Chem. Soc.*, **81**, 3510 (1959).

[19] P. Ausloos, *Can. J. Chem.*, **36**, 400 (1958).

[20] D. H. Derbyshire and E. W. R. Steacie, ibid., **32**, 457 (1954).

[21] It takes a time of the order of 10^{-11} sec. at ordinary temperatures for the two solute molecules enclosed together in a solvent cage to become separated from each other, provided that they do not react with each other (R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955)).