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The Studies of the Cage Effect of Solvents. VI. The Photolysis of Methylazoethane in *n*-Heptane

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Methylazoethane was photolyzed in *n*-heptane in order to study the effect of a solvent cage quantitatively; the results obtained were then compared with those for azomethane and azoethane previously studied. By using styrene as a scavenger for radicals, it was demonstrated that a large fraction (90% at −75°C and 58% at 100°C) of a pair of methyl and ethyl radicals formed by the decomposition of a molecule of methylazoethane combines to form propane or disproportionates to form methane and ethylene in an original solvent cage. The ratio of the rate constant for the disproportionation to that for the combination is small, and it decreases with a rise in the temperature, as was previously found for azoethane. The effect of the temperature on the yields of the products of cage reactions in the present work and in the previous work with azomethane and azoethane shows that the combination of ethyl radicals and the cross-combination of methyl and ethyl radicals in a solution require appreciable activation energies, even if that for the combination of methyl radicals is zero.

The photolysis of methylazoethane in a solution yields a pair of methyl and ethyl radicals in a solvent cage. The ratios of their subsequent combination and disproportionation have recently been investigated by Szwarc and his co-workers.¹⁾ In the present work, the photolysis of the same substrate in *n*-heptane has been studied in order to elucidate the general kinetics, including the cage reactions mentioned above, and in order to compare the results with those previously obtained for azomethane²⁾ and azoethane³⁾.

Experimental

Materials.—Methylazoethane was prepared by the thermal decomposition of the methylazoethane-cuprous chloride which had been obtained by the ethylation and oxidation of methylhydrazine sulfate,⁴⁾ in a way similar to that used for azomethane.⁵⁾ Since the prepared gas was about 2% azomethane, it was purified by a gas chromatographycal method with a column of dimethylformamide on activated alumina and was stored in a dark-colored reservoir. It was further purified before each use by condensation and evacuation at −140°C.

There has to date been no report on the properties of methylazoethane. We have now determined a few of them. The plot of the logarithmic vapor pressure vs. $1/T$ gives a good linear relation in the range from −48 to 20°C and is represented by $\log P = 7.78 - 1487/T$ The normal boiling point is calculated as 30.3°C from the equation. The molecular extinction coefficient, calculated from $\log(I/I_0) = -\varepsilon cd$ and with the optical densities determined in the gas phase, is illustrated in Fig. 1. The value for the absorption maximum situated at 352 mμ is 6.44 l. mol^{-1} cm^{-1}.

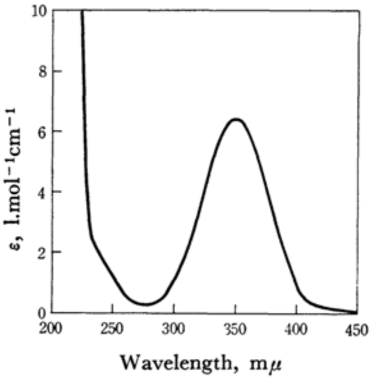

Fig. 1. Absorption spectrum of methylazoethane vapor at 29°C.

In this work *n*-heptane was used as the solvent for the reasons described in a previous paper³⁾ for azoethane, and styrene was used as the scavenger for radicals. They were taken from commercial samples which had been found to be gas chromatographically pure, and were subjected before use to thrice-repeated bulb-to-bulb distillation using a dry ice-acetone bath.

Procedure.—The apparatus was similar to that used for azomethane and previously described.²⁾ The reaction cells were glass cylinders about 3.6 cm. in diameter, 1.0 cm. long and about 10 cc. in volume. The full arc from a high-pressure mercury lamp, Mazda

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1) P. S. Dixon, A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 3344 (1963).

2) S. Kodama, This Bulletin, **35**, 652, 658, 824, 827 (1962).

3) S. Kodama, S. Fujita, J. Takeishi and O. Toyama, ibid., **39**, 1009 (1966).

4) H. H. Hatt, "Organic Syntheses," Coll. Vol. II, 395 (1943).

5) Ibid., Coll. Vol. II, 208 (1943); O. Diels and W. Koll, *Ann.*, **443** 262 (1925); F. P. Jahn, *J. Am. Chem. Soc.*, **59**, 1761 (1937).

Table I. Photolysis in the absence of styrene at 0°C

Time min.	Rate of formation ×10^{11} mol. cc^{-1} sec^{-1}					CH_4/N_2	C_2H_6/N_2	C_2H_4/N_2	C_3H_8/N_2	$(C_2H_4+C_3H_8)/N_2$	$(CH_4+C_3H_8)/N_2$	$(C_2H_6+C_2H_4+C_3H_8)/N_2$
	N_2	CH_4	C_2H_6	C_2H_4	C_3H_8	%	%	%	%	%	%	%
75a)	22.2	5.21	2.68	0.855	15.85	23.6	12.1	3.9	71.7	75.6	95.3	87.7
195a)	8.45	2.23	1.19	0.350	6.00	26.4	14.1	4.2	71.0	75.2	97.4	89.3
240b)	15.50	3.94	2.04	0.610	10.80	24.6	13.2	3.9	69.4	78.3	93.5	86.5
280b)	6.05	1.52	0.80	0.253	4.30	25.1	13.3	4.2	71.2	75.4	96.3	88.7

a) Without filter b) With filter

Table II. Photolysis in the presence of styrene

Temp. °C	CH_4/N_2 %	C_2H_4/N_2 %	C_3H_8/N_2 %	$(C_2H_4+C_3H_8)/N_2$ %	C_2H_4/C_3H_8 %
−75	5.55±0.30	6.00	83.5	89.5	7.2
−50	4.77±0.24	5.20±0.14	80.70±0.34	85.90	6.5
−25	4.40±0.27	4.5	76.70±0.34	81.20	5.9
0	3.67±0.12	4.03±0.09	72.90±0.20	76.93	5.5
25	3.65±0.24	3.70±0	68.9	72.60	5.4
50	3.87±0.19	—	—	—	—
75	4.15±0.10	2.70±0.14	60.5 ±1.0	63.2	4.5
100	4.55±0.24	2.50±0	55.30±0.41	57.80	4.5

Table III. Comparison of the three azo-compounds

Radical source	A_6/A_4	A_6/A_5	A_5/A_4	E_6-E_4 cal./mol.	E_6-E_5 cal./mol.	E_5-E_4 cal./mol.
Azomethane	4.32			1520		
Methylazoethane	3.86	134	0.026	1360	1760	−400
Azoethane	3.40	39.0	0.087	1050	1420	−370

SHL-100UV, was used for the photolysis in most experiments. The effective wavelength range seems to be restricted to 300—400 mμ, judging from the light absorption by methylazoethane and the transmission through the cell. In order to check the effect of the wavelength, a few experiments were carried out with a UV-Dl filter which transmits only the 366 mμ line. The extent of photolytic conversion in each run was usually about 5%. After the required time of irradiation, the reaction cell was opened to the analytical system, which consisted of traps set at −145°C and −210°C. The products of the photolysis were nitrogen, methane, ethane, ethylene and propane. After the gaseous components had been separated from the solution by thrice-repeated bulb-to-bulb distillation and by an autodistillation vessel[6)] at the dry ice-acetone temperature, methylazoethane was condensed at −145°C and ethane, ethylene and propane were trapped at −210°C. Noncondensable products, nitrogen and methane, were introduced into a Toepler guage and the volume of the mixture was determined. Each component was further analyzed by a gas chromatograph with a 2 m. silica gel column. The fraction trapped at −210°C was dealt with similarly. The column used for it was a series consisting of 2 m. of activated alumina with 2% squalane and 2 m. of ethylene glycol saturated with silver nitrate on celite at room temperature.

Results

Table I shows the results of photolysis in the absence of styrene at 0°C. As will be shown below, $(C_2H_4+C_3H_8)/N_2$ is a measure of the cage effect, and $(CH_4+C_3H_8)/N_2$ and $(C_2H_6+C_2H_4+C_3H_8)/N_2$ represent the material balances with reference to methyl and ethyl radicals respectively. It may be seen in the table that the irradiation of filtered light (366 mμ) produces little change in the yields of gaseous products, as would be expected from the effective wavelength range for the unfiltered light mentioned above. Table I further shows that the variation in light intensity or in the rate of nitrogen formation is almost without effect on the relative yields of gaseous products.

Table II shows the effect of the temperature in

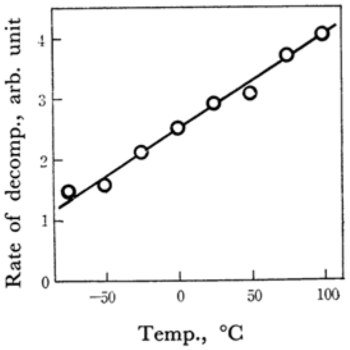

Fig. 2. Dependence of the decomposition rate on temperature.

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

the presence of styrene. The ethane yields were found to be negligible in this case; in the two runs carried out at −75 and 100°C, they were 0.21 and 0.48% respectively. The formation of butane was negligible even in the absence of styrene. Figure 2 shows the effect of the temperature on the rate of photolysis; this effect may be taken as reflecting the dependence of the quantum yield on the temperature, although the latter quantity was not measured in this work.

Discussion

Mechanism.—A comparison of the results obtained in this work with those previously obtained for azomethane[2)] and azoethane[3)] suggests that the following reaction scheme is probable for the present photolysis:

$$CH_3N_2C_2H_5 + h\nu \rightarrow CH_3N_2C_2H_5^* \qquad (1)$$

$$CH_3N_2C_2H_5^* + M \rightarrow CH_3N_2C_2H_5 + M \qquad (2)$$

$$CH_3N_2C_2H_5^* \rightarrow [CH_3 + N_2 + C_2H_5] \qquad (3)$$

$$[CH_3 + N_2 + C_2H_5] \rightarrow C_3H_8 + N_2 \qquad (4)$$

$$\rightarrow CH_4 + C_2H_4 + N_2 \qquad (5)$$

$$\rightarrow CH_3 + N_2 + C_2H_5 \qquad (6)$$

$$CH_3 + RH \rightarrow CH_4 + R \qquad (7)$$

$$C_2H_5 + RH \rightarrow C_2H_6 + R \qquad (8)$$

$$CH_3 \text{ (or } C_2H_5) + CH_3N_2C_2H_5 \rightarrow \text{addition products} \qquad (9)$$

$$CH_3 \text{ (or } C_2H_5) + R \rightarrow CH_3R \text{ or } (C_2H_5R) \qquad (10)$$

Reaction 1 represents the formation of excited molecules of the substrate by light absorption; reaction 2, their deactivation by solvent molecules, and reaction 3, the formation of a pair of methyl and ethyl radicals in a solvent cage by the decomposition of the excited molecule. Reactions 4 and 5 are, respectively, the combination and disproportionation of such a pair of radicals in the original solvent cage, while reaction 6 represents the separation of these radicals by diffusion prior to their combination or disproportionation. The remaining reactions are those for the methyl and ethyl radicals thus separated.

Figure 2 shows that the quantum yield of the photolysis falls off with a lowering of the temperature. Such a behavior is similar to that found for azoethane[3)] and may be accounted for by reactions 2 and 3, provided that the latter reaction requires an appreciable activation energy.

A comparison between Tables I and II shows that the yields of propane and ethylene are not affected by the presence of styrene, and that, consequently, these gaseous products are formed only by cage reactions 4 and 5. The sum of relative yields, $(C_3H_8 + C_2H_4)/N_2$, thus gives the fraction of the radicals that react in the solvent cage in reactions 4 and 5. Table II shows that this fraction is nearly 90% at −75°C, but that it falls to about 60% at 100°C, indicating that the escape of radicals from the solvent cage by diffusion is favored at elevated temperatures.

In the presence of a sufficient concentration of styrene, the reaction scheme given above requires that methane be formed solely by reaction 5, and that, consequently, the yield of methane equal that of ethylene. Table II shows that these yields are in fact nearly equal to each other at low temperatures, while above room temperature there is a substantial difference between them. This presumably indicates that, at high temperatures, a part of the methane comes from the hydrogen atom abstraction by the methyl radical from the solvent molecule constituting the cage.

A comparison between Tables I and II further shows that the yield of methane was reduced by the addition of from 25% to 4% of styrene at 0°C. Similarly, the yield of ethane was reduced from 13% to a negligibly small value at 0°C. These observations may be explained by reactions 7 and 8. As may be seen from the figures given above, the yield of methane in reaction 7 is higher than that of ethane in reaction 8. Consequently, the material balance for methyl radicals as represented by $(CH_4 + C_3H_8)/N_2$ is higher than that for ethyl radicals, $(C_2H_6 + C_2H_4 + C_3H_8)/N_2$ (Table I). These findings probably reflect the lesser ability of ethyl radicals to abstract hydrogen atoms from solvent molecules; this fact was previously inferred from the results of the photolysis of azoethane in solution.

The losses in the material balances for methyl and ethyl radicals may be accounted for by reactions 9 and 10. Their relative weights in importance are however not clear from this work.

Rate Constant Ratios of Cage Reactions.—When reactions 4—6 are regarded as ordinary elementary steps, it follows that:

$$k_5/k_4 = (C_2H_4)_s/(C_3H_8)_s$$

$$k_6/k_4 = [(N_2)_s - (C_2H_4)_s - (C_3H_8)_s]/(C_3H_8)_s$$

$$k_6/k_5 = [(N_2)_s - (C_2H_4)_s - (C_3H_8)_s]/(C_2H_4)_s$$

where the suffix s denotes the presence of styrene. On applying these equations to the experimental results, we obtain the Arrhenius plots shown in Figs. 3 and 4. The plot for k_5/k_4 is linear, but those for k_6/k_4 and k_6/k_5 show deviations above room temperature, as was the case with azoethane. These deviations presumably arise from the inadequacy of the crude representation given in reaction 6 for the escape of radicals from a solvent cage at high temperatures.

Table III shows the Arrhenius parameters determined from Figs. 3 and 4; for the latter figure these quantities refer to the linear portions of the plots. The table also contains the corresponding

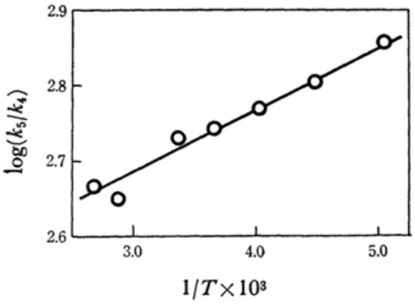

Fig. 3. Arrhenius plot for k_5/k_4.

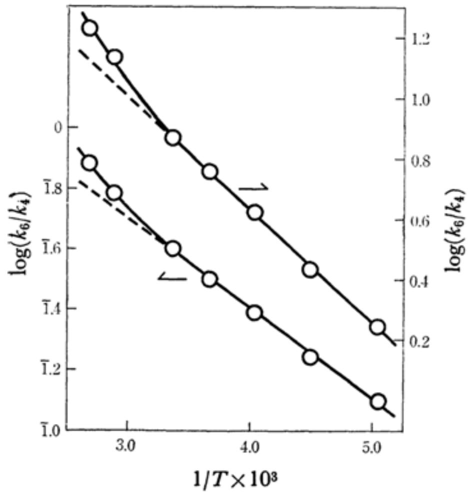

Fig. 4. Arrhenius plots for k_6/k_4 and k_6/k_5.

values for azomethane⁷⁾ and azoethane³⁾. It may be seen in the table that E_5-E_4 is slightly negative for methylazoethane as well as for azoethane. These results are in agreement with those obtained and discussed in detail by Szwarc and his co-workers.[1,8]

The energy differences, E_6-E_4 and E_6-E_5, on the other hand, are definitely positive, indicating that the effect of the temperature on the cage reactions is largely controlled by the energy of activation for the diffusion of radicals.

Table III shows that E_6-E_4 decreases in the order of azomethane, methylazoethane, and azoethane. If the value of E_4 were zero for all of the methyl-methyl, methyl-ethyl and ethyl-ethyl combination, the trend in the values of E_6-E_4 would mean a greater activation energy for the diffusion of methyl radicals than that for ethyl radicals, contrary to what would be expected. Table III, therefore, leads to the conclusion that the combination of ethyl radicals and the cross-combination of methyl and ethyl radicals require activation energies greater than about 0.5 and 0.2 kcal./mol. respectively at least. This conclusion is compatible with previously-reported values. The activation energy for the combination of ethyl radicals has been reported as 2 kcal./mol. in the gas phase[9] and as 0.8 kcal./mol. in solution,[10] while that for methyl radicals is regarded as approximately zero in the gas phase.[11]

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[7] In the previous work with azomethane no experiment was carried out in *n*-heptane. The values for azomethane listed in the table are those determined in this work by photolyzing azomethane in *n*-heptane.

[8] M. Matsuoka, P. S. Dixon, A. P. Stefani and M. Szwarc, *Proc. Chem. Soc.*, 304 (1962); P. S. Dixon, A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551 (1963).

[9] A. Shepp and O. K. Kutschke, *J. Chem. Phys.*, **26**, 1020 (1957).

[10] R. W. Fessenden and R. H.Schuler, ibid., **39**, 2147 (1963).

[11] R. Gomer and G. B. Kistiakowsky, ibid., **19**, 85 (1951); G. B. Kistiakowsky and E. K. Roberts, ibid., **21**, 1637 (1953); A. Shepp, ibid., **24**, 939 (1956).