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Studies of the Cage Effect of Solvents. V. The Photolysis of Azoethane in *n*-Heptane

By Sukeya KODAMA, Shin'ichi FUJITA, Junsuke TAKEISHI and Osamu TOYAMA

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka

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The effect of a solvent cage on the photolysis of azoethane in *n*-heptane was investigated at 366 mμ in the temperature range from -75 to 99°C. Among the gaseous products, nitrogen served as a measure of the azoethane decomposed. The other gaseous products were *n*-butane, ethane and ethylene; these three hydrocarbons accounted for ninety per cent of the decomposition at 0°C. The quantum yield of nitrogen was found to decrease with a lowering of the temperature. The value obtained at 0°C was 0.021. In the presence of a sufficient amount of styrene, which was used as a scavenger for ethyl radicals, the yields of the gaseous hydrocarbons were more or less reduced to constant values; from these the ratio of rate constants for the combination and disproportionation of the geminate ethyl radicals formed by the photolysis in a solvent cage was determined to be $k_{\text{comb}}/k_{\text{disp}}=11.5\exp(-371/\boldsymbol{R}T)$. The fraction of ethyl radicals that reacted in these ways in the solvent cage, before escaping it, was dependent on the temperature; it decreased from 0.838 at -75°C to 0.467 at 99°C. In the absence of styrene, the reactions for ethyl radicals that escaped the original solvent cages were inferred to be hydrogen abstraction, addition, combination and disproportionation.

In previous papers of the present series,[1] the effect of a solvent cage on the geminate methyl radicals formed by the photolysis of azomethane in various solvents was reported on. This paper will report on a similar study of the ethyl radicals obtained by the photolysis of azoethane in *n*-heptane.

The cage effect in the photolysis of azoethane in solution has been investigated by Szwarc and his co-workers[2] in an attempt to determine the ratio of disproportionation to combination of the geminate ethyl radicals in a solvent cage, and in an attempt to compare the results with those obtained in the gas phase. The present work will provide quantitative data that will enable us to discuss the reactions in the solvent cage in relation to the other reactions involved in the photolysis.

Experimental

Materials.—Azoethane was prepared by the thermal decomposition of the azoethane - cuprous chloride obtained from diethyl hydrazine di-hydrochloride and then purified and stored in a way similar to that used for azomethane.[1a] The solvent used in this work was *n*-hepane. It was chosen for various reasons: *n*-butane, a major product in the photolysis, is separated with ease from *n*-heptane by fractional distillation; the ethyl radicals formed in the photolysis would not be consumed in the addition reaction to solvent molecules if the latter had no double bonds; and the rate of the photolysis of azoethane would be reduced if the solvent were polar.[3] *n*-Heptane, obtained as a commercial sample, was found to be gas chromatographically pure. It was, however, further purified by vacuum distillation before use.

The scavenger used in this work for ethyl radicals was styrene, which was used in the previous work for methyl radicals. Commercial styrene was purified by vacuum distillation.

Apparatus and Procedure.—The photolysis was carried out with a solution of about 0.05 M azoethane in *n*-heptane at 366 mμ, using a high-pressure mercury lamp of 100 W. (Mazda SHL-100UV) and a glass filter (Mazda UV-Dl). In a few experiments, the filter was removed to obtain a high-intensity light. In experiments with varied light intensity, screens were used to reduce the light intensity. The reaction cell was a glass cylinder of 3.6 cm. in diameter and 1.0 cm. long, with a capacity of about 10 ml. The other details about the apparatus and the procedure have been described in a previous paper.[1a]

The gaseous products were nitrogen, ethylene, ethane and *n*-butane. These were separated from the solution by thrice-repeated bulb-to-bulb distillation at the dry ice - acetone temperature. For *n*-butane, an automatic fractional distillation vessel was used. Undecomposed azoethane, heptane vapor and by-products were separated by a column of cuprous chloride crystals at -120°C. This column reduced the vapor pressure of azoethane by forming an addition compound in the way opposite to that described above for preparing azoethane and enabled us to separate butane from azoethane at -120°C. The addition and release processes of azoethane on the column were reversible at a reduced pressure. *n*-Butane was condensed at

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[1] a) S. Kodama, This Bulletin, **35**, 652 (1962); b) ibid., **35**, 658 (1962); c) ibid., **35**, 824 (1962); d) ibid., **35**, 827 (1962).

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

[3] Such tendency has been found for the photolysis of azomethane (Refs. 1b and 1c).

TABLE I. PHOTOLYSIS OF AZOETHANE IN *n*-HEPTANE AT 366 mμ

Temp.	$\frac{[C_6H_5C_2H_3]}{[C_7H_{16}]}$	Reac. time	Rate of formation × 10^{11} mol. cc^{-1} sec^{-1}				$\frac{C_2H_4}{N_2}$	$\frac{C_2H_6}{N_2}$	$\frac{C_4H_{10}}{N_2}$	$\frac{1/2(C_2H_4+C_2H_6)+C_4H_{10}}{N_2}$	$\left(\frac{C_4H_{10}+C_2H_4}{N_2}\right)_S$	$\frac{C_2H_4}{C_4H_{10}}$
°C	%	min.	R_{N_2}	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	%	%	%	%	%	%
0	0	240	7.86	0.91	3.44	4.84	11.6	43.8	61.6	89.3		18.8
0	0	125[a]	18.1	1.96	7.61	11.3	10.8	42.0	62.3	88.7		17.3
0	0	120	19.3	2.12	8.01	12.2	11.0	41.5	63.0	89.3		17.4
0	0	80[a]	39.6	4.87	15.6	25.5	12.3	39.4	64.3	90.2		19.1
0	0	75[a]	46.7	5.60	17.5	30.8	12.0	37.6	66.0	90.8		18.2
0	0.116	120	17.9	1.95	2.90	—	10.9	16.2	—		—	—
0	0.348	120	16.7	1.75	2.14	9.95	10.5	12.8	59.6		70.1	17.6
0	1.15	120	19.9	2.05	2.29	—	10.3	11.5	—		—	—
0	2.38	120	19.8	2.12	2.12	11.9	10.7	10.7	60.3		71.0	17.8
0	4.22	120	18.4	1.95	1.97	11.1	10.6	10.7	60.1		70.6	17.6
0	6.05	95[a]	40.2	4.10	4.34	24.2	10.2	10.8	60.2		70.4	17.0
0	6.05	135	19.3	2.05	2.05	11.6	10.6	10.6	60.1		70.7	17.6
−75	6.0	190	12.1	1.84	1.90	8.29	15.2	15.7	68.5		83.8	22.2
−50	6.0	180	11.8	1.57	1.64	7.81	13.3	13.9	66.2		79.8	20.1
−25	6.0	180	13.9	1.63	1.72	8.74	11.7	12.4	62.8		74.5	18.6
25	6.0	121	16.6	1.53	1.69	9.40	9.2	10.2	56.6		65.8	16.3
50	6.0	120	12.9	1.04	1.20	6.66	8.1	9.3	51.7		59.8	15.6
62	6.0	170	20.5	1.57	1.69	10.1	7.7	8.3	49.5		57.1	15.4
75	6.0	120	7.20	0.50	0.61	3.37	7.0	8.4	46.8		53.7	14.8
87	6.0	170	25.8	1.61	2.03	—	6.2	7.9	—		—	—
90	6.0	170	15.9	1.09	1.25	6.87	6.5	7.9	43.2		49.7	15.0
99	6.0	120	23.5	1.36	1.70	9.62	5.8	7.2	40.9		46.7	14.2

a) Without filter

−165°C, while ethane and ethylene were condensed at −210°C. The noncondensed nitrogen was determined by a Toepler gauge. The ethane and ethylene were determined by the Toepler gauge and a gas chromatograph with a column of 2% squalane on activated alumina (2 m.) and ethylene glycol saturated with silver nitrate on celite (2 m.) at room temperature. The Toepler gauge was also used to determine the *n*-butane.

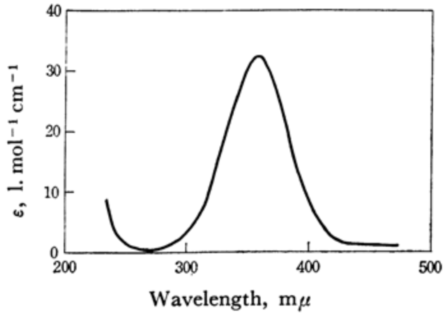

Fig. 1. Absorption curve of azoethane in *n*-heptane.

The molecular extinction coefficient of azoethane in *n*-heptane was determined to be as shown in Fig. 1. The quantum yield of nitrogen formation was measured by using a potassium ferrioxalate actinometer[4] and a quartz reaction cell. The value obtained at 366 mμ was 0.021 at 0°C.

Results

Table I summarizes the results obtained. The rates of the formation of the various products given in the table refer to the initial conversion of a small percentage. The $[1/2(C_2H_4+C_2H_6)+C_4H_{10}]/N_2$ column represents the material balance which takes only these products into account, since one molecule of azoethane gives one molecule of nitrogen and two ethyl radicals, the latter of which combine to butane or produce ethylene and ethane. The $[(C_2H_4+C_4H_{10})/N_2]_s$ column represents the sum of the yields of ethylene and butane relative to that of nitrogen in the presence of a sufficient amount of styrene; it gives, as is shown below, the fraction of ethyl radicals that undergo cage reactions.

Figure 2 shows the dependence of the yields of butane, ethane and ethylene and the material balance on the rate of photolysis, i. e., on the light intensity, in the absence of styrene at 0°C. Figure 3 shows the effect of the addition of styrene in increasing amounts at 0°C. Figures 2 and 3 both show that the result of photolysis is scarcely influenced at all by removing the light filter. This indicates that the most effective mercury line is 366 mμ, as would be expected from the absorption curve given in Fig. 1 and from the absorption property of the glass reaction cell.

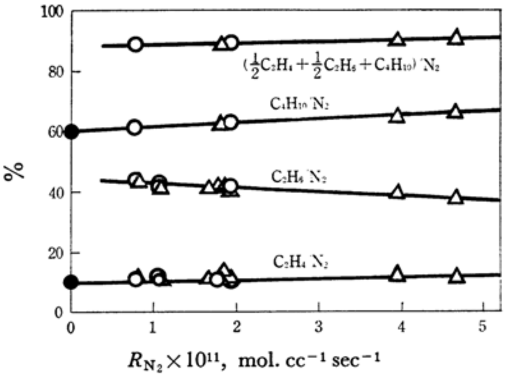

Fig. 2.
○, at 366 mμ; △, without filter; ●, in presence of styrene

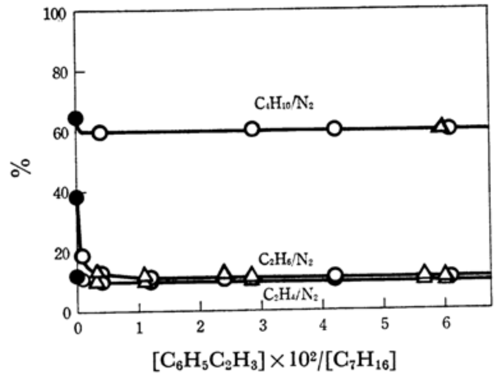

Fig. 3. Effect of styrene on the photolysis at 0°C.
○, at 366 mμ; △, without filter; ●, in absence of styrene, at $R_{N_2}=4\times10^{-11}$ mol. cc⁻¹ sec⁻¹

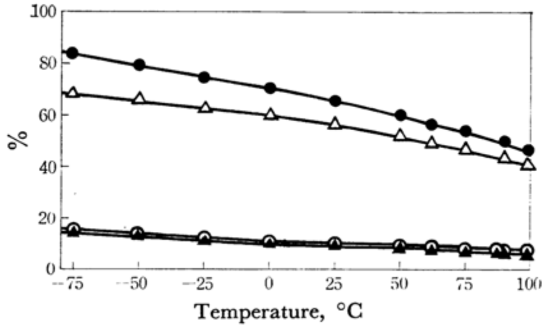

Fig. 4. Effect of temperature on the photolysis in the presence of styrene.
●, $[(C_4H_{10}+C_2H_4)/N_2]_s$; △, $(C_4H_{10}/N_2)_s$;
○, $(C_2H_6/N_2)_s$; ▲, $(C_2H_4/N_2)_s$

Figure 4 shows the effect of the temperature on the photolysis in the presence of styrene. Figure 5 shows the effect of the temperature on the quantum yield of nitrogen at 366 mμ. This curve was

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[4] C. A. Parker, *Proc. Roy. Soc.*, **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, ibid., **235**, 518 (1956).

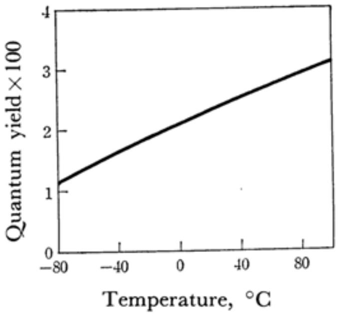

Fig. 5. Dependence of quantum yield on temperature.

drawn by comparing the rates of nitrogen formation at various temperatures, keeping the azoethane concentration and light intensity constant and normalizing them to the quantum yield value of 0.021 at 0°C.

Discussion

Primary Processes.—Previous studies of the photolysis of azoethane in the gas phase[5] and of azomethane in solution[1] suggest that the probable processes in the initial stage of the present photolysis may be:

$$\mathrm{C_2H_5N_2C_2H_5} + h\nu \rightarrow \mathrm{C_2H_5N_2C_2H_5^*} \tag{1}$$

$$\mathrm{C_2H_5N_2C_2H_5^*} + \mathrm{M} \rightarrow \mathrm{C_2H_5N_2C_2H_5} + \mathrm{M} \tag{2}$$

$$\mathrm{C_2H_5N_2C_2H_5^*} \rightarrow [\mathrm{2C_2H_5} + \mathrm{N_2}] \tag{3}$$

Here the asterisk denotes the excited state; M, a solvent molecule, and the bracketed species, those formed together in a solvent cage.

Cerfontain and Kutschke[5e] have shown that, in the gas phase photolysis of azoethane as well as in that of azoisopropane, the excited molecules of the substrate are deactivated by collision, while such deactivation is absent in the case of azomethane. Reaction 2, therefore, cannot be omitted in the present case, though a corresponding deactivation process was previously neglected in the photolysis of azomethane in solution.[1]

Reaction 2 appears to account for the result that the quantum yield of nitrogen is considerably less than unity. However, the quantum yield falls off with a lowering of the temperature, as is shown in Fig. 5, while the studies of the yield of fluorescence in solution show that the quenching by deactivation usually increases with the temperature.[6] If reaction 2 is the only process involved in reducing the quantum yield, the decomposition of the excited azoethane must require an appreciable energy of activation.

The decomposition of the excited molecules of azoethane is represented in reaction 3 as a one-step act. If, however, they decompose in two stages, as $\mathrm{C_2H_5N_2C_2H_5^*} \rightarrow \mathrm{C_2H_5N_2} + \mathrm{C_2H_5}$ followed by $\mathrm{C_2H_5N_2} \rightarrow \mathrm{C_2H_5} + \mathrm{N_2}$, the recombination reaction, $\mathrm{C_2H_5N_2} + \mathrm{C_2H_5} \rightarrow \mathrm{C_2H_5N_2C_2H_5}$, in a solvent cage may provide an alternative explanation for the low quantum yield of nitrogen. Such a possibility can not be ruled out, though the decomposition of the $\mathrm{C_2H_5N_2}$ radicals has been inferred to be considerably exothermic[7] and the flash photolysis technique has as yet given no evidence for the formation of this species as a transient intermediate.[5d,5f]

The short-lived $\mathrm{C_2H_5N_2}$ radicals, if formed, would not survive to take part in reactions other than the decomposition and recombination considered above. So far as the secondary reactions to be discussed below are concerned, therefore, the decomposition of the excited azoethane may virtually be represented by reaction 3.

Cage Reactions.—In view of the reactions between ethyl radicals in the gas phase, the probable reactions for the geminate ethyl radicals formed by reaction 3 may be :

$$[\mathrm{2C_2H_5} + \mathrm{N_2}] \rightarrow \mathrm{C_4H_{10}} + \mathrm{N_2} \tag{4}$$

$$\rightarrow \mathrm{C_2H_6} + \mathrm{C_2H_4} + \mathrm{N_2} \tag{5}$$

$$\rightarrow \mathrm{2C_2H_5} + \mathrm{N_2} \tag{6}$$

Reactions 4 and 5 are, respectively, the combination and disproportionation of the geminate ethyl radicals in the original solvent cage, while reaction 6 represents the separation of the radicals from each other by their escaping the cage before they combine or disproportionate.

Figure 3 shows that, in the presence of a sufficient amount of styrene as a scavenger for ethyl radicals, almost all the butane, ethane and ethylene are formed by the cage reactions 4 and 5.[8] However, in Fig. 3 as well as in Fig. 4, the yield of ethane in the presence of styrene is slightly higher than that of ethylene, whereas they should be equal to each other according to reaction 5. It seems possible that this slight difference arises from the hydrogen atom abstraction by hot ethyl radicals from the solvent molecules constituting the cages, since the excess energy released by the decomposition of azoethane amounts to 62 kcal./mol. at 366 mμ.

The fraction of the geminate ethyl radicals that react in the solvent cage as represented in reactions 4 and 5 may be computed from the sum of the

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5) a) J. L. Weiniger and O. K. Rice, *J. Am. Chem. Soc.*, **74**, 6216 (1953); b) P. Ausloos and W. R. Steacie, *Bull. soc. chim. Belges.*, **63**, 87 (1954); c) H. Cerfontain and O. K. Kutschke, *Can. J. Chem.*, **36**, 344 (1958); d) B. C. Roquitte and J. H. Futrell, *J. Chem. Phys.*, **37**, 378 (1962); e) H. Cerfontain and O. K. Kutschke, *J. Am. Chem. Soc.*, **84**, 4017 (1962); f) D. P. Dingledy and J. G. Calvert, ibid., **85**, 856 (1963).

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

7) B. G. Gowenlock, J. R. Majer and D. R. Snelling, *Trans. Faraday Soc.*, **58**, 670 (1962).

8) The direct formation of these compounds from azoethane by a molecular rearrangement has been shown to be negligible (Refs. 5e and 5f).

relative yields $(C_4H_{10}+C_2H_4)/N_2$ in the presence of styrene. Figure 4 shows that this fraction is greater than 0.8 below −50°C, but that it decreases with a rise in the temperature, reflecting the fact that the escape of the ethyl radical from the solvent cage by diffusion is favored at high temperatures.

The Reactions of Ethyl Radicals That Have Escaped the Original Cages.—The results obtained in the present work, together with those obtained previously in the photolysis of azomethane in solution,¹⁾ suggest that the probable reactions for the ethyl radicals that have escaped the original cages are:

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \tag{7}$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4 \tag{8}$$

$$C_2H_5 + RH \rightarrow C_2H_6 + R \tag{9}$$

$$C_2H_5 + (C_2H_5)_2N_2 \rightarrow (C_2H_5)_3N_2 \tag{10}$$

RH in reaction 9 represents a molecule of *n*-heptane, the solvent. The hydrogen atom abstraction from azoethane molecules by ethyl radicals may not be important, because its rate constant may be of the same order of magnitude as that for reaction 9, while the concentration of azoethane in the present experiment is as low as 0.05 mol./l.

The difference between the results obtained with and without styrene is accounted for by reactions 7—10. Figures 2 and 3 show that ethane formed in other ways than reaction 5 is largely due to reaction 9. Figure 2, however, shows that, as the rate of nitrogen formation increases, i. e., as the concentration of ethyl radicals increases, the yield of ethane falls off, while those for butane and ethylene increase. These observations may be explained as follows. As the concentration of ethyl radicals increases, the rates of combination and disproportionation increase; both of these rates are second-order with respect to ethyl radicals and have very low activation energies. This, in turn, reduces the fraction of ethyl radicals consumed in reaction 9, which is first-order in the ethyl radical and which has a considerable activation energy.⁹⁾ For a similar reason, the fraction of ethyl radicals consumed in reaction 10 is also reduced; this improves, though slightly, the material balance given in Fig. 2 as the concentration of ethyl radicals increases.

It cannot be concluded from the present work that only reaction 10 is responsible for the material balance less than unity, represented by $[1/2(C_2H_4+C_2H_6)+C_4H_{10}]/N_2$. Another possibility may be $C_2H_5+R \rightarrow C_2H_5R$. However, a combination $R+R \rightarrow R_2$ is also a probable reaction for the solvent radical R. It will, however, be tentatively assumed below that the loss in material balance arises mostly from reaction 10.

In the previous studies with azomethane,¹⁾ the combination of methyl radicals corresponding to reaction 7 was found to be negligible compared to the hydrogen atom abstraction reaction similar to reaction 9. This difference probably reflects the lower ability of ethyl radicals in solution to abstract hydrogen atoms from solvent molecules.

The Evaluation of the Rate Constant Ratios.—A steady-state treatment of reactions 1—3, combined with the dependence of the quantum yield of nitrogen on the temperature (Fig. 5), yields:

$$k_3/k_2 = 0.5 \exp(-650/\boldsymbol{R}T) \text{mol. l}^{-1} \tag{I}$$

A corresponding expression for the gas-phase photolysis has been obtained as:¹⁰⁾

$$0.25 \exp(-2000/\boldsymbol{R}T) \text{mol. l}^{-1}$$

Reactions 4—6, when regarded as ordinary elementary steps, lead to:

$$k_4/k_5 = (C_4H_{10})_s/(C_2H_4)_s \tag{II}$$

$$k_6/k_4 = [(N_2)_s - (C_4H_{10})_s - (C_2H_4)_s]/(C_4H_{10})_s \tag{III}$$

$$k_6/k_5 = [(N_2)_s - (C_4H_{10})_s - (C_2H_4)_s]/(C_2H_4)_s \tag{IV}$$

where the suffix s denotes the presence of styrene. The Arrhenius plots of these rate constant ratios are shown in Fig. 6. The plot for Eq. II is linear and yields:

$$k_4/k_5 = 11.5 \exp(-371/\boldsymbol{R}T) \tag{V}$$

The rate constant ratio for the disproportionation and combination of ethyl radicals as given

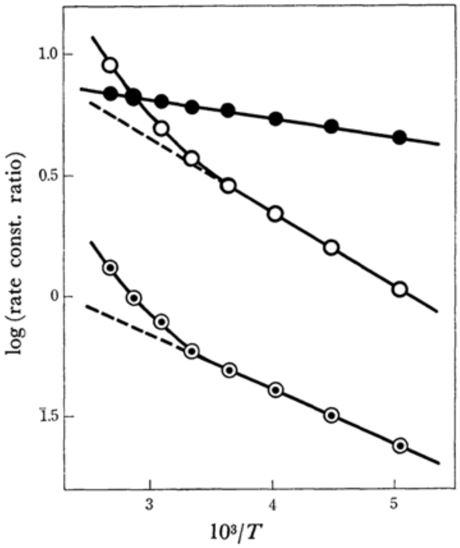

Fig. 6. Arrhenius plots of rate constant ratio. ●, k_4/k_5; ○, k_6/k_5; ⊙, k_6/k_4

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9) A reported value in the gas phase is 10.6 kcal./mol. (D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc.*, **A244**, 289 (1958)).

10) Calculated from the results obtained by Cerfontain and Kutschke (Ref. 5c).

by the C_2H_4/C_4H_{10} ratio of yields has been investigated by many workers in the gas phase. The most reliable value given by these studies is 0.13 ± 0.02; it is independent of the temperature in the 50—250°C range.[2b,5f] All the values of $(C_2H_4)_s/(C_4H_{10})_s$ given in Table I are greater than 0.13, and Eq. V shows that k_4/k_5 is slightly dependent on the temperature. Similar results have been obtained and discussed in detail by Szwarc and his co-workers.[2]

Figure 6 shows that the plots for Eqs. III and IV are not linear above room temperature. Similar deviations at high temperatures were observed in the photolysis of azomethane in solution.[1d] The Arrhenius plots for the self-diffusion in such liquids as *n*-pentane and *n*-heptane also show anomalies at high temperatures.[11] As was described in a previous paper on the photolysis of azomethane,[1d] the crude representation for the escape of a radical from a solvent cage given in reaction 6 seems to break down at high temperatures, giving rise to these deviations.

The linear portions of the plots for k_6/k_4 and k_6/k_5 below room temperature yield:

$$k_6/k_4 = 3.40 \exp(-1050/\boldsymbol{R}T) \qquad \text{(VI)}$$

$$k_6/k_5 = 39.0 \exp(-1420/\boldsymbol{R}T) \qquad \text{(VII)}$$

The significance of these expressions will be discussed in a later paper, together with the results obtained in the photolysis of $CH_3N_2C_2H_5$ in solution.

The yields of butane, ethane and ethylene formed by reactions 7—9 are given by comparing each yield in the presence of and in the absence of styrene. The yield for reaction 10 is obtained as $2-(2C_4H_{10}+C_2H_6+C_2H_4)/N_2$. By combining these quantities, we obtain the following values at 0°C:

$$k_9/k_7^{1/2} = 1.2\times 10^{-4}\ \mathrm{l}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{sec}^{-1/2}$$

$$k_{10}/k_7^{1/2} = 1.1\times 10^{-2}\ \mathrm{l}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{sec}^{-1/2}$$

$$k_{10}/k_9 = 93$$

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11) E. Fishman, *J. Phys. Chem.*, **59**, 469 (1955)