Studies of the Cage Effect of Solvent. III. Photolysis of Azomethane in Frozen Solutions

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Previous studies of the photolysis of azomethane in *n*-hexane,[1] *n*-octane, toluene, ethyl acetate and ethanol[2] have suggested that a pair of methyl radicals formed by the decomposition of a substrate molecule combine to form an ethane molecule with a high yield in the solvent cage. The yield of ethane has been found to increase with the lowering of the temperature, and it may be expected that still higher yields would be obtained in frozen solutions if the ethane were formed in the way given above.

This paper reports on experiments carried out to investigate the effect of such freezing as well as to obtain additional results in various other solvents than those already studied. The solvents used are cyclohexane, benzene, styrene, *o*-xylene and *tert*-amyl alcohol.

Experimental

The preparation, purification and storage of azomethane have been described previously[1]. Cyclohexane obtained from a commercial sample of a special high grade was boiled with stannous chloride and hydrochloric acid and then distilled. Benzene, styrene, *o*-xylene and *tert*-amyl alcohol were taken from commercial samples of a special high grade without further purification. All these solvents, as well as azomethane, were subjected to vacuum distillation each time befor use.

The apparatus and procedure have been described in a previous paper[1]. The concentration of azomethane was about 3×10^{-2} mol./l. in all the experiments, and the volume of solution was adjusted so that it just filled the reaction cell of ca. 10 ml. capacity at the temperature of photolysis. A mercury line of 366 mμ was used for the photolysis. The extent of conversion in each run was within several percentage points. Nitrogen, methane and ethane, produced by the photolysis, were analyzed in the way that has been described previously[1].

Results and Discussion

The results obtained are shown in Figs. 1—6. As has been described in previous papers[1,2], CH_4/N_2, C_2H_6/N_2 and $[(1/2)CH_4+C_2H_6]/N_2$ represent respectively the yields of methane and ethane and the material balance referring to them. The main feature of the photolysis in the liquid phase is, as seen in the figures, similar to that found previously for a number of other solvents[1,2]. Hence, the mechanism of the photolysis in the liquid solutions here studied may be envisaged as the same as in the previous work. The formation of ethane may thus be ascribed to the cage combination of a pair of methyl radicals resulting from the decomposition of the substrate molecule, and that of methane, mostly to the hydrogen atom abstraction from the solvent molecules by methyl radicals that have escaped the original solvent cage.

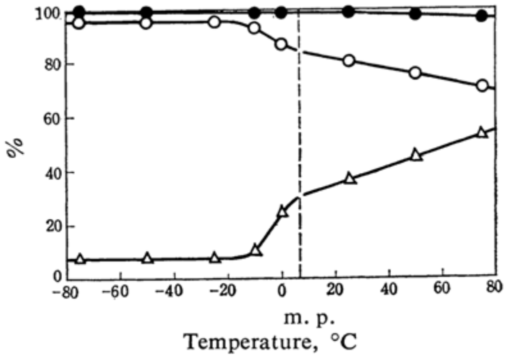

Fig. 1. Effect of freezing on yields of methane and ethane, and material balance in cyclohexane.
△, CH_4/N_2; ○, C_2H_6/N_2;
●, $[(1/2)CH_4+C_2H_6]/N_2$

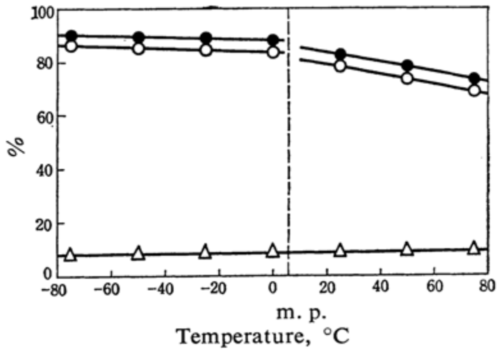

Fig. 1. Effect of freezing on yields of methane and ethane, and material balance in benzene.
△, CH_4/N_2; ○, C_2H_6/N_2;
●, $[(1/2)CH_4+C_2H_6]/N_2$

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[1] S. Kodama, This Bulletin, 35, 652 (1962).
[2] S. Kodama, ibid., 35, 658 (1962).

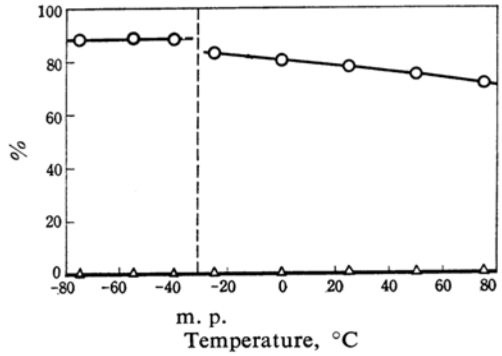

Fig. 3. Effect of freezing on yields of methane and ethane in styrene.

△, CH_4/N_2; ○, C_2H_6/N_2

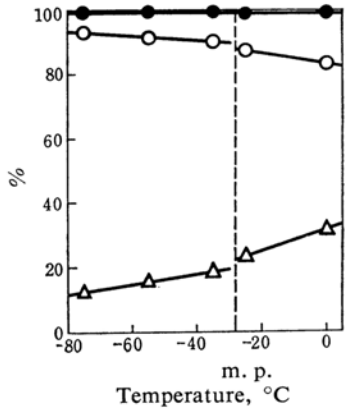

Fig. 4. Effect of freezing on yields of methane and ethane, and material balance in *o*-xylene.

△, CH_4/N_2; ○, C_2H_6/N_2;
●, $[(1/2)CH_4+C_2H_6]/N_2$

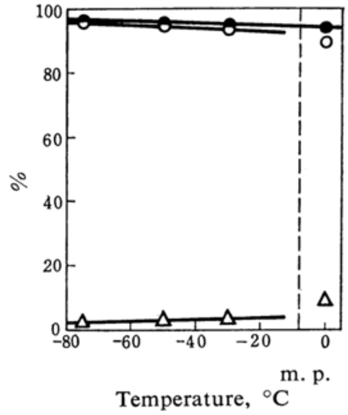

Fig. 5. Effect of freezing on yields of methane and ethane, and material balance in *t*-amyl alcohol.

△, CH_4/N_2; ○, C_2H_6/N_2;
●, $[(1/2)CH_4+C_2H_6]/N_2$

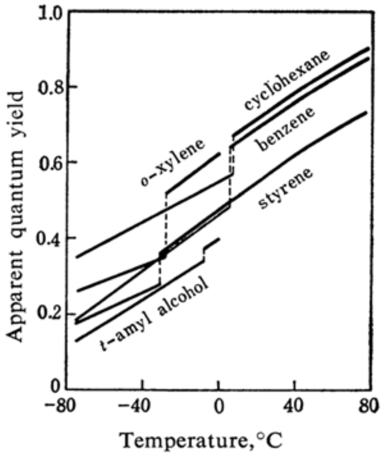

Fig. 6. Apparent quantum yields.

Figures 1—5 show that, on freezing the solution, the yield of ethane is more or less enhanced, while that of methane is mostly reduced. Such a result is in agreement with what is to be expected if the ethane is formed in the way described above, for in the frozen solutions the two methyl radicals formed by the photolysis from an azomethane molecule would not diffuse away from each other with such ease as in liquid solutions.

As the temperature is further lowered, however, the methyl radicals would become more and more immobile, and the yield of ethane would then be determined by the geometrical arrangement of the three fragments produced by the photolysis and by the structure of the environment, rather than by the rate of escaping diffusion of methyl radicals. The small dependence of the yields of ethane and methane in frozen solutions upon temperature as seen in Figs. 1—5 appears to reflect the small variation in the structure of the solid with variations in temperature, as supposed from far smaller expansion coefficients of solids than those of liquids. It seems, however, probable that, in the experiments at very low temperatures, both ethane and methane are partly formed from methyl radicals mobilized on warming up the reaction cell after irradiation.

Frozen solutions are, on the other hand, probably heterogeneous, solute molecules aggregating in boundaries between grains of the frozen solvent. Although it is not feasible to observe the effect of such a heterogeneous structure separately, the variation in the velocity of freezing would lead to different structures and hence, possibly, to different results. Table I shows the results of such experiments carried out with cyclohexane as a solvent. In Runs 1 and 2, the solution was frozen by immersing the cell in liquid nitrogen

TABLE I. PHOTOLYSIS OF AZOMETHANE IN CYCLOHEXANE AT 0°C

Run No.	Time of irradiation	Rate of formation $\times 10^{10}$ mol. sec^{-1}			CH_4/N_2	C_2H_6/N_2	$\frac{1}{2}CH_4+C_2H_6$/N_2
	min.	R_{N_2}	R_{CH_4}	$R_{C_2H_6}$	%	%	%
1	42	22.6	5.33	19.7	23.6	87.2	99.0
2	90	21.3	4.35	18.6	20.4	87.2	97.4
3	66	20.8	4.33	18.1	20.8	87.0	97.4

and in dry ice-acetone respectively, and then warmed to 0°C without melting. In Run 3 the solution was simply cooled from room temperature to 0°C and frozen at the latter temperature. As seen in the table, the yields of ethane in these three runs are identical, though the yield of methane is slightly higher in the solution frozen with liquid nitrogen. The cage combination of methyl radicals thus appears to be rather insensitive to the heterogeneity considered above.

As is seen in Fig. 1, the results obtained with cyclohexane show some anomalies below its melting point; the yields of ethane and methane reflect less sharply the transition from liquid to solid, compared to the other solutions. On inspecting the reaction cell, it was found that the front surface of the frozen solution was melted under irradiation, presumably because of the low heat of the fusion of cyclohexane[3]. It is, therefore, most probable that such partial melting gave rise to the above anomalous behavior in the experiments with cyclohexane.

The results obtained with styrene are of interest in view of its large methyl affinity[4]. In the previous work performed with various solvents, it was used as a scavenger of methyl radicals escaping from the solvent cage. Figures 1—5 show that the yield of ethane in styrene is, in the liquid phase as well as in the solid, of a magnitude comparable to those in the other solvents. This is not an unexpected result, because the scavenging reaction of styrene requires the activation energy of some 5 kcal./mol.[2], while that of the combination of methyl radicals is nearly zero. Figure 3 shows further that the formation of methane is suppressed almost completely in styrene in both the liquid and the solid phases, which may be accounted for by the greater activation energy of the abstraction reaction than that of the addition[5]. The difference $1—C_2H_6/N_2$ in this case may therefore be taken approximately as the fraction of methyl radicals used in the addition to styrene. Such addition may in turn be expected to induce the polymerization of styrene. In the experiments carried out at high temperatures, it has been observed that such polymerization really takes place.

Benzene has also a fairly large methyl affinity[6] owing to its unsaturated structure, and may be expected to show the effect of the addition reaction. The results given in Fig. 2 show that the addition competes with the abstraction, but the effects of temperature on the two reactions suggest that their Arrhenius parameters are appreciably different. By applying the same method as has been described previously[2], the difference in activation energies can be computed as

$$E_{\text{addition}} - E_{\text{abstraction}} = 1.5 \text{ kcal./mol.}$$

Figure 4 shows that, though *o*-xylene also has double bonds, the contribution of the addition reaction is negligible. On the other hand, Fig. 5 shows a rather large loss in the material balance, though *tert*-amyl alcohol has no double bond. Presumably, impurities in the alcohol have given rise to the loss of methyl radicals in this case.

It has been found in the previous work[1,2] that the variation in the yields of ethane in various solvents can be represented by an empirical equation

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

wherer A and E are constants. Figure 7 shows that this equation also conforms to the results in the liquid solutions in this work. Table II gives the values of the constants A and E obtained from the figure.

Figure 6 shows the apparent quantum yields obtained by comparing the rates of formation

TABLE II. ARRHENIUS CONSTANTS

	A	E kcal./mol.
Cyclohexane	3.62	1.74
Benzene	2.61	1.48
Styrene	1.06	0.93
o-Xylene	2.10	1.39

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3) The heat of fusion of cyclohexane is 0.6398 kcal./mol., which is much lower than the 2.361 kcal./mol. for benzene and the 3.250 kcal./mol. for *o*-xylene. (F. D. Rossini et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press (1953)).

4) 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).

5) Although the activation energy of the hydrogen atom abstraction from styrene molecules by methyl radicals is unknown, most reported values for hydrogen atom abstraction by methyl radicals are greater than 8 kcal./mol.

6) M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); M. Levy, M. Steinberg and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 3439 (1954).

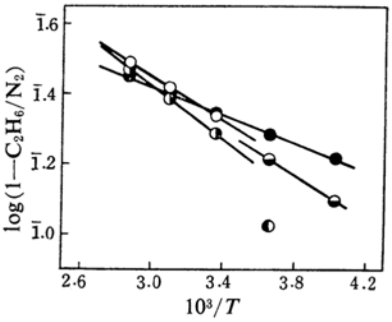

Fig. 7 Arrhenius plots of $1-C_2H_6/N_2$.
◑, Cyclohexane ; ○, Benzene ;
●, Styrene ; ◒, *o*-Xylene ;
◐, *tert*-Amyl alcohol

of nitrogen. They all decrease with the lowering of the temperature, as has been found previously(1,2), and are, on freezing the solutions, lowered discontinuously, which may be ascribed to reduced absorption of light by the frozen solution as well as to the increased recombination of a pair of initially formed radicals, CH_3N_2 and CH_3(1). It has been found in the previous work(2) that the apparent quantum yield is low in polar solvents. Figure 6 shows a similar tendency in this work.

Summary

The photolysis of azomethane has been studied in cyclohexane, benzene, styrene, *o*-xylene and *tert*-amyl alcohol in the temperature range both above and below the freezing point of a given solution. The results obtained in the liquid solutions are essentially similar to those previously obtained with other solvents, except for styrene. The photolysis in the latter differs in that it gives little methane because of the strong scavenging action of styrene. Nevertheless, ethane with a yield comparable to those in the other solvents is formed even in styrene. It has been found with all the solutions investigated that the yield of ethane is more or less enhanced by freezing. All these findings provide additional evidence that the ethane is formed by the cage combination of a pair of methyl radicals resulting from the decomposition of a substrate molecule. For all the solvents investigated, the temperature dependence of the yield of ethane in the liquid phase conforms to the empirical equation previously presented. The apparent quantum yields obtained by comparing the rates of formation of nitrogen decrease with the lowering of the temperature, as was found previously.

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