Studies of the Cage Effect of Solvent. II. Photolysis of Azomethane in Various Solvents

By Sukeya KODAMA

(Received August 31, 1961)

It has been reported in a previous paper[1] that ethane, a major product in the photolysis of azomethane in *n*-hexane, is formed exclusively by the combination of a pair of methyl radicals resulting from the substrate molecule in the solvent cage. The photolysis of azomethane in solution thus provides a good example of the cage effect that can be studied quantitatively.

This paper reports the results of a series of experiments carried out to investigate the dependence of the above cage combination of methyl radicals on the nature of the solvent. The solvents selected were *n*-octane, ethanol, ethyl acetate and toluene. They are widely different from each other in molecular structure and in property, and all of them are transparent to the 366 mμ used for the photolysis.

Experimental

The preparation, purification and storage of azomethane have previously been described[1]. *n*-Octane was prepared from *n*-butyl bromide by the Wurts reaction and purified in a way similar to that described for *n*-hexane. Ethanol, ethyl acetate and styrene, used as a scavenger of methyl radicals, were all taken from commercial samples of a special high grade and were used without further purification. Toluene, also obtained from a commercial sample, was boiled with anhydrous aluminium chloride, washed with water, repeatedly shaken with concentrated sulfuric acid until the latter was not colored, washed with a solution of sodium carbonate and with water, dried over calcium chloride and phosphorus pentoxide, and distilled. All the solvents thus obtained were subjected to thrice repeated vacuum distillation each time before use.

The apparatus and procedure were similar to those previously described[1]. A mercury line of 366 mμ was used for the photolysis throughout the whole series of experiments. The extent of conversion in each run was usually less than 4%. In the experiments with toluene it was less than 7%. The concentration of azomethane in each run was fixed at about 3×10^{-2} mol./l., because the previous study showed little dependence of yields of products on the substrate concentration. The volume of the solution in each experiment was adjusted so that it just filled the reaction cell of ca. 10 ml. capacity at the experimental temperature.

1) S. Kodama, This Bulletin, 35, 652 (1962).

Results

Tables I—IV and Figs. 1 and 2 show the results obtained. CH_4/N_2 and C_2H_6/N_2 represent the yields of methane and ethane respectively, since the number of moles of nitrogen formed is equal to that of the azomethane decomposed. $((1/2)CH_4+C_2H_6)/N_2$ gives the material balance referring to methane and ethane.

Figure 3 shows the apparent quantum yields obtained by comparing the rate of formation of nitrogen in a given solution with that in *n*-hexane solution, for which the apparent quantum yield is already known[1].

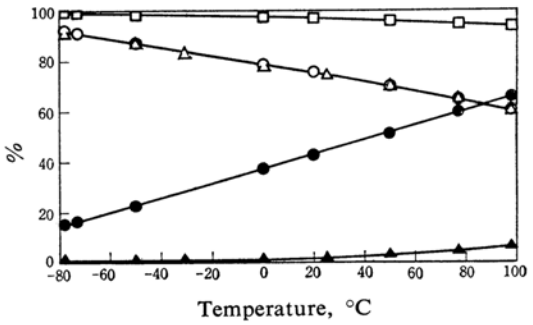

Fig. 1. Effect of temperature on yields of methane and ethane, and material balance in ethyl acetate. ○, C_2H_6/N_2; △, $(C_2H_6/N_2)_S$; ●, CH_4/N_2; ▲, $(CH_4/N_2)_S$; □, $((1/2)CH_4+C_2H_6)/N_2$

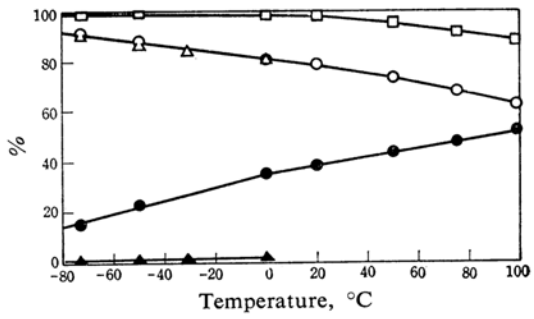

Fig. 2. Effect of temperature on yields of methane and ethane, and material balance in toluene. ○, C_2H_6/N_2; △, $(C_2H_6/N_2)_S$; ●, CH_4/N_2; ▲, $(CH_4/N_2)_S$; □, $((1/2)\cdot CH_4+C_2H_6)/N_2$

TABLE I. PHOTOLYSIS OF AZOMETHANE IN ETHYL ACETATE

Temp. °C	$[C_6H_5C_2H_3]/[CH_3COOC_2H_5]$ %	Time of irradiation min.	Rate of formation $\times 10^{10}$ mol. sec^{-1}			CH_4/N_2 %	C_2H_6/N_2 %	$(1/2)CH_4+C_2H_6/N_2$ %
			R_{N_2}	R_{CH_4}	$R_{C_2H_6}$			
98	0	60	35.0	23.0	21.3	65.8	60.7	93.9
98	2.42	60	32.1	2.00	19.4	6.22	60.6	
77	0	54	31.8	19.0	20.6	59.8	64.8	94.7
77	2.42	72	35.4	1.52	22.9	4.30	64.7	
50	0	60	22.8	11.7	15.9	51.2	69.8	95.9
50	2.42	78	26.0	0.69	18.2	2.65	70.0	
25	2.42	72	19.6	0.29	14.7	1.50	74.8	
20	0	60	17.2	7.37	13.0	42.8	75.7	97.1
0	0	60	27.0	10.2	21.3	37.6	78.8	97.6
0	2.42	72	28.3	0.28	22.0	1.0	77.8	
−31	2.42	78	18.2	0.15	15.1	0.8	83.0	
−50	0	90	15.1	3.41	13.1	22.6	87.0	98.3
−50	2.42	90	13.3	0.09	11.5	0.7	86.6	
−73	0	120	2.42	0.40	2.20	16.4	91.0	99.2
−78	0	120	9.04	1.36	8.31	15.1	92.0	99.6
−78	2.42	120	9.55	0.07	8.65	0.7	90.6	

TABLE II. PHOTOLYSIS OF AZOMETHANE IN ETHANOL

Temp. °C	$[C_6H_5C_2H_3]/[C_2H_5OH]$ %	Time of irradiation min.	Rate of formation $\times 10^{10}$ mol. sec^{-1}			CH_4/N_2 %	C_2H_6/N_2 %	$(1/2)CH_4+C_2H_6/N_2$ %
			R_{N_2}	R_{CH_4}	$R_{C_2H_6}$			
78	0	72	16.2	9.05	11.3	55.8	70.0	97.9
50	0	90	15.9	7.83	11.8	49.2	74.1	98.7
20	0	120	12.5	5.05	9.88	40.4	79.0	99.2
0	0	60	17.7	6.38	14.4	36.0	81.5	99.5
0	1.42	108	17.1	0.58	13.9	3.4	81.2	
−31	1.42	102	11.3	0.23	9.68	2.0	85.7	
−50	0	60	8.93	2.09	7.88	23.4	88.2	99.9
−50	1.42	108	9.02	0.17	8.00	1.9	88.7	
−68	1.42	66	7.07	0.12	6.41	1.7	90.7	
−73	0	120	7.92	1.44	7.20	18.2	90.8	99.9

TABLE III. PHOTOLYSIS OF AZOMETHANE IN TOLUENE

Temp. °C	$[C_6H_5C_2H_3]/[C_6H_5CH_3]$ %	Time of irradiation min.	Rate of formation $\times 10^{10}$ mol. sec^{-1}			CH_4/N_2 %	C_2H_6/N_2 %	$(1/2)CH_4+C_2H_6/N_2$ %
			R_{N_2}	R_{CH_4}	$R_{C_2H_6}$			
98.5	0	48	37.0	19.3	23.1	52.2	62.5	88.6
75	0	48	32.1	15.4	21.8	47.9	67.9	91.9
50	0	54	29.9	13.1	22.0	43.9	73.5	95.5
20	0	54	25.8	9.96	20.4	38.6	79.0	98.3
0	0	60	42.9	15.2	34.7	35.4	81.0	98.7
0	2.55	60	41.2	0.86	33.1	2.1	80.3	
−31	2.55	60	30.2	0.42	25.4	1.4	84.0	
−50	0	60	23.3	5.36	20.6	23.0	88.4	99.9
−50	2.55	60	23.3	0.28	20.0	1.2	86.4	
−73	0	180	21.6	3.26	19.8	15.1	91.6	99.2
−73	2.55	90	17.2	0.21	15.6	1.2	90.8	

TABLE IV. PHOTOLYSIS OF AZOMETHANE IN *n*-OCTANE

Temp. °C	Time of irradiation min.	Rate of formation $\times 10^{10}$ mol. sec^{-1}			$\frac{CH_4}{N_2}$ %	$\frac{C_2H_6}{N_2}$ %	$\frac{(1/2)CH_4+C_2H_6}{N_2}$ %
		R_{N_2}	R_{CH_4}	$R_{C_2H_6}$			
98	42	45.8	32.1	26.7	70.2	58.3	93.4
75	42	42.2	26.5	26.8	62.8	63.5	95.0
50	48	39.7	21.5	27.5	54.2	69.3	96.5
25	48	33.4	15.4	25.1	46.0	75.1	98.1
0	60	27.9	10.0	22.3	36.0	80.1	98.6
−25	60	27.9	8.13	23.6	29.1	84.5	99.0
−50	72	25.7	5.14	22.9	20.0	89.2	99.2

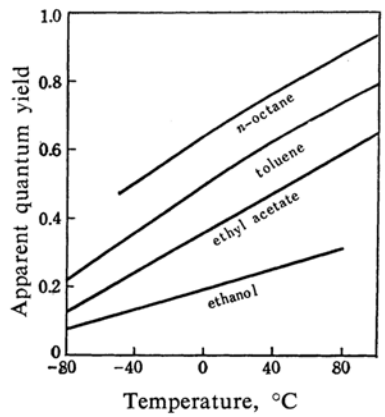

Fig. 3. Dependence of apparent quantum yield on temperature in various solvents.

Discussion

A comparison of the results given in Tables I—IV and Figs. 1 and 2 with those obtained with *n*-hexane[1] shows that the main feature of the photolysis is not affected by the nature of the solvent. Hence, on similar grounds to those previously given, the formation of the main products, i. e., nitrogen, methane and ethane, may be represented as:

$$(CH_3)_2N_2+h\nu \rightarrow [2\,CH_3+N_2] \quad (1)$$

$$[2\,CH_3+N_2] \rightarrow C_2H_6+N_2 \quad (2)$$

$$\rightarrow CH_3+N_2+CH_3 \quad (3)$$

$$CH_3+HR \rightarrow CH_4+R \quad (4)$$

where the parenthesis denotes the solvent cage and HR, the solvent. The hydrogen atom abstraction from azomethane molecules by methyl radicals may be far less important compared to reaction 4. Again, the loss in the material balance, $1-((1/2)CH_4+C_2H_6)/N_2$, may be ascribed to addition reactions such as

$$CH_3+(CH_3)_2N_2 \rightarrow (CH_3)_3N_2 \quad (5)$$

$$CH_3+R \rightarrow CH_3R \quad (6)$$

and the suppression of the formation of methane by styrene to

$$CH_3+S \rightarrow CH_3S \quad (7)$$

where S represents styrene.

As seen in Fig. 3, the quantum yield falls off with a lowering of the temperature in all the solvents investigated; this phenomenon may be ascribed to the recombination of a pair of initially formed radicals, CH_3N_2 and CH_3, in the solvent cage, as previously inferred for the *n*-hexane solution. What the different apparent values of the quantum yield shown in the figure have resulted from cannot be answered for the present. It may be that the absorption curve of azomethane in solution is different from solvent to solvent, but measurements of this have not yet been reported. It may, however, be noted that these apparent quantum yields have some correlation with the dipole moments of the solvents. The latter values are 0(*n*-octane), 0.4(toluene), 1.70 (ethanol) and 1.74 *D*(ethyl acetate); in Fig. 3 the apparent quantum yield increases in reverse order, except for ethanol. The apparent quantum yields in *n*-hexane[1], *n*-octane and cyclohexane[2], whose dipole moments are all zero, have been found to be almost identical at all the temperatures investigated. Ethanol, which apparently gives an exceptionally low quantum yield, is well-known by its tendency to form the hydrogen bond. A comparison of the results given in Tables I—IV with those previously obtained with *n*-hexane shows that the yield of ethane and its dependence on the temperature are rather insensitive to the nature of the solvent. As shown in Fig. 4, the results obtained with various solvents can all be represented by an empirical formula

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

which has been previously found to be applicable to the results obtained with *n*-hexane. The values of the constants *A* and *E* determined from these plots are given in Table V, together with those for *n*-hexane[3]. It is seen that the

2) S. Kodama, ibid., to be published.

3) Although the quantity $1-C_2H_6/N_2$ represents the fraction of methyl radicals that escaped the solvent cage, the constant *E* cannot be taken as the diffusion energy of methyl radicals in solution, as was pointed out in the previous paper.

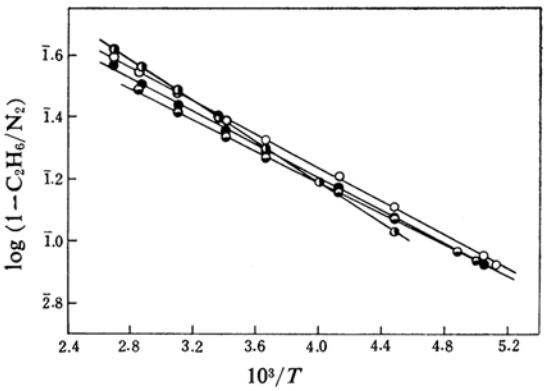

Fig. 4. Arrhenius plots of $1-C_2H_6/N_2$. ○, ethyl acetate; ◒, ethanol; ●, toluene; ◑, *n*-octane.

TABLE V. VALUES OF ARRHENIUS CONSTANTS OBTAINED FROM FIG. 4

Solvent	A	E kcal./mol.
Ethyl acetate	2.22	1.29
Ethanol	1.48	1.12
Toluene	1.90	1.24
n-Octane	2.40	1.51
n-Hexane	2.08	1.17

dependence of the constants A and E on the nature of the solvent is rather small, as has been stated above.

The yield of methane shows a somewhat greater dependence on the nature of the solvent. As has already been described, the values of the material balance $((1/2)CH_4+C_2H_6)/N_2$ show that a small fraction of the methyl radicals is probably lost by addition reactions. Consequently, the greater the number of methyl radicals lost in this way, the lower is the yield of methane. Table III and Fig. 2 show that the relatively low yield of methane above room temperature in the case of toluene arises from a relatively large loss of methyl radicals, which loss may be ascribed to the contribution of the addition of methyl radicals to toluene molecules taking place in this case in addition to those already given. On the other hand, the relatively low yields of methane found with ethanol result from relatively high yields of ethane and not from enhanced addition reactions.

In the presence of styrene as a scavenger, it competes with the solvent for methyl radicals. Accordingly, it follows in the steady state that

$$k_7/k_4=R_{CH_3S}/R_{CH_4}\cdot[HR]/[S]$$

where R's denote respective rates and k's, rate constants. The ratio R_{CH_3S}/R_{CH_4} is obtained by

$$R_{CH_3S}/R_{CH_4}=[(CH_4/N_2)_0-(CH_4/N_2)_S]/(CH_4/N_2)_S$$

where $(CH_4/N_2)_S$ represents the yield of methane in the presence of styrene and $(CH_4/N_2)_0$, that in its absence. Consequently,

$$k_7/k_4=[(CH_4/N_2)_0-(CH_4/N_2)_S]/(CH_4/N_2)_S\cdot[HR]/[S]$$

If, therefore, the rate constant k_4 is known, k_7 is obtained from the observed values of $(CH_4/N_2)_0$ and $(CH_4/N_2)_S$. This is the same principle as that applied by Szwarc[4] to determine the methyl affinities of various compounds in the thermal decomposition of acetyl peroxide.

For the solvents here investigated, exact Arrhenius expressions of k_4 are unknown, but they are expected to have similar activation energies. Figure 5 shows the Arrhenius plots of k_7/k_4 for the results obtained with ethyl acetate and with *n*-hexane[1]. The two plots are parallel to each other and, accordingly, give the same value of 3.2 kcal./mol. for E_4-E_7. The value of E_4 for *n*-hexane is reported as 8.1 kcal./mol.[5] E_7 is therefore obtained as 4.9 kcal./mol.

Figure 5 shows that the frequency factor of the hydrogen atom abstraction from *n*-hexane molecules by methyl radicals is about four times as great as that for ethyl acetate. This can be explained if secondary hydrogen atoms are preferentially abstracted, since the ratio of the number of secondary hydrogen atoms in the two kinds of molecule is just four[6].

The value of 3.2 kcal./mol. found above for

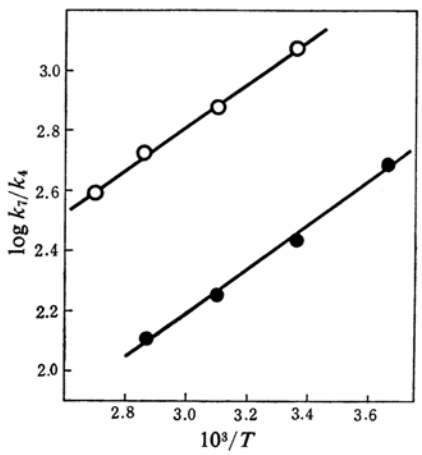

Fig. 5. Arrhenius plots of k_7/k_4 for the results obtained with ethyl acetate and *n*-hexane. ○, ethyl acetate; ●, *n*-hexane.

4) M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); *J. Am. Chem. Soc.*, **77**, 1949 (1955).

5) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

6) It has been found that the rate of hydrogen atom abstraction by methyl radicals depends on the nature of the hydrogen atom abstracted, and, in general, the order of the reactivity of hydrogen atoms is tertiary>secondary >primary (R. K. Brinton, *Can. J. Chem.*, **38**, 1339 (1960)).

E_4-E_7 is in good agreement with the result obtained by Szwarc[7] with isooctane. However, the reported values of the ratio of rate constants k_7/k_4 in the latter case are higher than those for ethyl acetate shown in Fig. 5. This is contrary to what would be expected, since the isooctane molecule has a tertiary hydrogen atom in addition to as many secondary hydrogen atoms as the ethyl acetate molecule. The reason for this discrepancy is not clear.

Summary

The photolysis of azomethane in *n*-octane, toluene, ethyl acetate and ethanol has been investigated over the temperature range from about −80 to 100°C. The results obtained are very similar to those previously obtained with *n*-hexane and show that, also in these solvents, the ethane, one of the main products, exclusively results from the combination in the solvent cage of a pair of methyl radicals formed from an azomethane molecule. For all the solvents investigated, the temperature dependence of the yield of ethane referred to nitrogen formed, C_2H_6/N_2, can be represented by an empirical expression, $1-C_2H_6/N_2=A\exp(-E/RT)$, with constants A and E, whose values are rather insensitive to the nature of the solvent. From the reduction of the yield of methane in the presence of styrene, the activation energy of the addition of methyl radicals to styrene molecules is estimated as 4.9 kcal./mol. Apparent quantum yields obtained by comparing the rates of formation of nitrogen fall off with a lowering of the temperature in all the solvents investigated.

The present author is particularly indebted to Professor Osamu Toyama of the College of Engineering for his discussions and encouragement during this investigation. The author wishes also to thank Mr. Katsuji Makino for his assistance.

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

7) M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 3791 (1960).