Studies of the Cage Effect of Solvent. IV. Dependence of the Cage Combination of Methyl Radicals on Solvent and on Temperature

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It has been shown in a previous paper[1] that the photolysis of azomethane in *n*-hexane provides a good example of the cage combination of methyl radicals that can be studied quantitatively. This photolysis has further been studied with various other solvents, and the results obtained have subsequently been reported[2,3]. This paper presents a discussion of these results with reference to the dependence of the cage combination of methyl radicals on solvent and on temperature.

Experimental Results

The solvents in which the photolysis of azomethane has been studied are *n*-hexane[1], *n*-octane[2], benzene[3], toluene[2], styrene[3], *o*-xylene[3], cyclohexane[3], ethyl acetate[2], ethanol[2] and *tert*-amyl alcohol[3]. The photolysis was conducted by the irradiation of a mercury line of 366 mμ throughout all the experiments. Some experiments were also carried out with

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[1] S. Kodama, This Bulletin, 35, 652 (1962).
[2] S. Kodama, ibid., 35, 658 (1962).
[3] S. Kodama, ibid., 35, 824 (1962).

313 mμ in *n*-hexane[1], but they gave no appreciably different results. The range of the extent of conversion in the runs was usually within several percentage points.

The main products of the photolysis have always been found to be nitrogen, methane and ethane. It has been shown by a scavenger technique using styrene that all the ethane formed by the photolysis can be attributed to the cage combination of a pair of methyl radicals resulting from the decomposition of a substrate molecule[1,2]:

$$(CH_3)_2N_2 + h\nu \rightarrow [2CH_3 + N_2] \tag{1}$$

$$[2CH_3 + N_2] \rightarrow C_2H_6 + N_2 \tag{2}$$

(Here the parentheses denote the solvent cage.) The results obtained with a scavenger show, on the other hand, that the formation of methane is explained by the hydrogen atom abstraction from a solvent molecule by a methyl radical that has escaped the cage:

$$[2CH_3 + N_2] \rightarrow CH_3 + N_2 + CH_3 \tag{3}$$

$$CH_3 + HR \rightarrow CH_4 + R \tag{4}$$

where HR represents a solvent molecule. The material balance referring to nitrogen, methane and ethane, however, indicates that a small fraction of the methyl radicals, increasing in quantity with the temperature, yields other products than methane, presumably by various addition reactions.

Since the rate of photolysis is given by that of the formation of nitrogen, the ratio of the amount of ethane formed to that of nitrogen, C_2H_6/N_2, represents the yield of ethane. According to the mechanism given above, this yield of ethane represents the probability of the cage combination of a pair of methyl radicals produced in the solvent cage. It has been confirmed by experiment that the yield of ethane in a given solvent is affected neither by the rate of photolysis nor by the concentration of substrate, but is dependent only on the temperature. Figure 1 shows the effect of the temperature on the yield of ethane for the various solvents investigated[4]. The figure shows only results obtained in liquid solutions. For some of these solvents, the photolysis in frozen solutions has been studied[3]; the yield of ethane is more or less enhanced on freezing the solution, and the yield in the frozen solution is far less dependent on the temperature than in the liquid. These results are not illustrated here, however, because they have no direct relation to the present discussion.

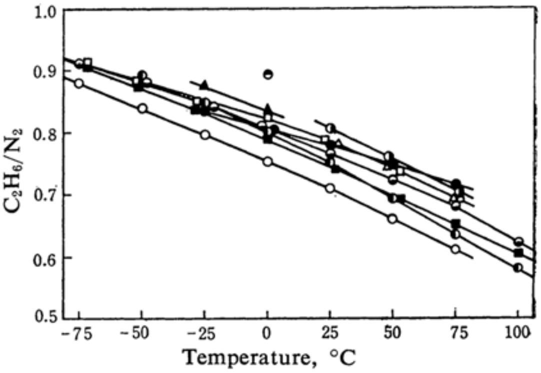

Fig. 1. Yields of ethane obtained with various solvents. ○, *n*-Hexane; ◐, *n*-Octane; ◑, Cyclohexane; ◒, Toluene; ◓, *tert*-Amyl alcohol; ●, Styrene; △, Benzene; ▲, *o*-Xylene; □, Ethanol; ■, Ethyl acetate

In this paper viscosity is shown to be an important property of the solvent influencing the yield of ethane. Table I gives the parameters for the expression $\eta = \eta_0 \exp(E_\eta/RT)$, where η is the viscosity of the solvent. These values were all obtained from Arrhenius plots of the viscosities measured in this work in the temperature range 0 to 60°C, because the solvents used in this work might not always have been pure. For *tert*-amyl alcohol viscosity was measured only at 0°C, with the result that $\eta = 0.1168$ poise. The viscosity values obtained for *n*-octane, ethanol, cyclohexane, benzene, toluene and styrene were in good agreement with those previously reported, while for *o*-xylene, ethyl acetate and *tert*-amyl alcohol somewhat higher values were obtained. *n*-Hexane showed considerably higher values than those in the literature, presumably because the sample used had been prepared from petroleum and so contained higher hydrocarbons, even after purification. All the viscosity values used in the following discussion have been calculated from Table I.

TABLE I. ARRHENIUS PARAMETERS FOR VISCOSITIES OF SOLVENTS

Solvent	$\eta_0 \times 10^5$ poise	E_η cal./mol.
n-Hexane	28.84	1500
n-Octane	14.09	2125
Ethyl acetate	17.23	1920
Ethanol	3.33	3430
Cyclohexane	5.05	3060
Benzene	11.94	2315
Toluene	16.00	2100
o-Xylene	7.18	2720
Styrene	12.82	2380

Discussion

Table II shows the yields of ethane compared with some properties of solvents. The yield

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[4] The yields of ethane given in the figure for respective temperatures have been obtained from smoothed curves.

TABLE II. COMPARISON OF YIELDS OF ETHANE WITH SOME PROPERTIES OF SOLVENTS

Solvent	Mol. wt.	Density at 25°C	Viscosity $\times 10^3$ poise at 25°C	Dipole moment D	C_2H_6/N_2 at 25°C	C_2H_6/N_2 at 0°C
n-Hexane	86.2	0.6545	3.70	0	0.710	0.752
Ethyl acetate	88.1	0.8985	4.43	1.74	0.742	0.787
n-Octane	114.2	0.6984	5.11	0	0.751	0.802
Toluene	92.1	0.8623	5.52	0.4	0.766	0.808
Styrene	104.2	0.9010	7.11	0.15	0.780	0.808
Benzene	78.1	0.8733	5.94	0	0.783	
Ethanol	46.1	0.7847	10.57	1.70	0.787	0.823
o-Xylene	106.2	0.8760	7.22	0.52		0.835
Cyclohexane	84.2	0.7738	8.81	0	0.806	
t-Amyl alcohol	88.2	0.8047	30.9			0.894

TABLE III. ARRHENIUS PARAMETERS FOR EQS. I AND II

Solvent	A_{I}	E_{I} kcal./mol.	A_{II}	E_{II} kcal./mol.	E_{D} kcal./mol.
n-Hexane	2.08	1.17	3.42	1.27	2.07
n-Octane	2.40	1.51	6.60	1.78	2.42
Ethyl acetate	2.22	1.29	3.84	1.44	
Ethanol	1.48	1.12	2.30	1.28	4.50
Cyclohexane	3.62	1.74			4.56
Benzene	2.61	1.48			2.00
Toluene	1.90	1.24	2.55	1.29	
o-Xylene	2.10	1.39	4.22	1.66	
Styrene	1.06	0.93	1.42	0.972	

TABLE IV. β' VALUES FOR $a=1.80\,\text{Å}$

Solvent	β' Lowest temp.	β' 0°C	β' Highest temp.
n-Hexane	0.988 (−75°C)	0.960	0.920 (75°C)
n-Octane	0.990 (−50°C)	0.973	0.915 (100°C)
Ethyl acetate	0.993 (−75°C)	0.968	0.911 (100°C)
Ethanol	0.999 (−75°C)	0.990	0.955 (75°C)
t-Amyl alcohol		0.998	
Cyclohexane	0.977 (25°C)		0.950 (75°C)
Benzene	0.966 (25°C)		0.938 (75°C)
Toluene	0.995 (−75°C)	0.975	0.922 (100°C)
o-Xylene	0.990 (−25°C)	0.982	
Styrene	0.988 (−25°C)	0.980	0.947 (75°C)

appears to depend on the viscosity of the solvent rather than on any other property. However, the differences in the yields are not large, and both the yield and viscosity are dependent on the temperature. No reliable conclusion can, therefore, be drawn from the table.

It has previously been found$^{1-3)}$ that the variation in the yield of ethane with the temperature, as shown in Fig. 1, conforms to the following equation for all the solvents investigated:

$$C_2H_6/N_2 = 1 - A_{\mathrm{I}} \exp(-E_{\mathrm{I}}/\boldsymbol{RT}) \qquad \text{(I)}$$

where A_{I} and E_{I} are constants dependent on the nature of the solvent. In Table III are listed the values of these constants determined for various solvents. The constants A_{I} and E_{I} thus reflect the specific behavior of each solvent towards the cage combination of methyl radicals and appear at first sight to deserve further discussion. Nevertheless, unfortunately, the equation is merely an empirical one, and hence neither A_{I} nor E_{I} is a well defined quantity.

The mechanism of the photolysis represented by reactions 1−4 gives only a crude picture of what would really take place; reactions 2 and 3 would actually involve sequences of complicated diffusive displacements in a system where methyl radicals are surrounded by solvent molecules of complex structure and with variable configurations and orientations. The situation thus appears to be intractable to any simple theoretical treatment.

The simplest way to interpret the data obtained in this work may be to treat reactions 2 and 3 as though they were elementary processes[1]. This is probably an over-simplification in view of the argument given above, but it may be of some interest to see what is obtained by the application of such a treatment. Reactions 2 and 3 give in the steady state

$$(1-C_2H_6/N_2)/(C_2H_6/N_2)=k_3/k_2 \qquad \text{(II)}$$

where k_2 and k_3 are the respective rate constants. It is generally accepted that two methyl radicals in contact with each other require no activation energy to combine. If, therefore, the chance for such a contact in the cage can be assumed to be approximately independent of the temperature, k_3 would be a constant. Then the Arrhenius plot of the quantity on the left-hand side of the above equation would give the activation energy of reaction 3, which may approximately be taken as the diffusion energy of methyl radicals in solution. Figure 2 shows, however, that actually most such plots have bends at about 25°C. It may be expected that the simplified treatment applied here deviates more from reality with a rise in temperature. In Table III are, therefore, listed the Arrhenius parameters A_{II} and E_{II} determined from linear plots in the low temperature range. As seen in the table, these values differ not greatly from those obtained by Eq. I. E_{II} values are lower than the corresponding diffusion energies of solvents given together in the table. The present work gives no evidence to justify the simple treatment applied here, but these low E_{II} values would not necessarily contradict the interpretation that E_{II} represents approximately the diffusion energy of methyl radicals in solution, since the diffusion energies given in the table are those for self-diffusion[5].

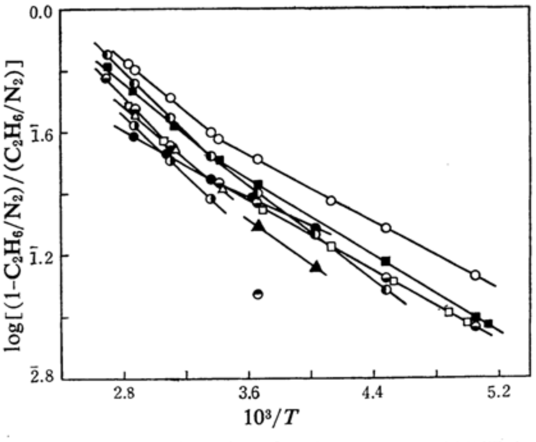

Fig. 2. Arrhenius plots for $(1-C_2H_6/N_2)/(C_2H_6/N_2)$. ○, *n*-Hexane; ◐, *n*-Octane; ◑, Cyclohexane; ◒, Toluene; ◓, *tert*-Amyl alcohol; ●, Styrene; △, Benzene; ▲, *o*-Xylene; □, Ethanol; ■, Ethyl acetate

Another approach to the problem being considered has been given by Noyes[6]. He has derived a theoretical expression for the quantum yield of the photolysis of iodine in solution, assuming that the solvent can be treated as a viscous continuum in which iodine atoms displace by diffusion. The comparison between the theory and experiment has shown that the theory gives rather satisfactory results. The following is an attempt to apply Noyes's theory to the present photolysis, though such a treatment here meets various difficulties.

According to Noyes, if β_0' is the probability that two iodine atoms whose centers were initially separated by a distance s_t will ultimately combine with each other,

$$\beta_0'=2a\beta'/s_t \qquad \text{(III)}$$

where a is the radius of the iodine atom and β', the probability that two atoms which were initially in contact with each other will recombine if they separate with an average thermal kinetic energy. The distance of the initial separation s_t is given by

$$s_t=2a+(m\varepsilon)^{1/2}/(3\pi\eta a) \qquad \text{(IV)}$$

where m is the mass of an iodine atom, η the viscosity of solvent, and ε the kinetic energy with which two iodine atoms separate in opposite directions. Equations III and IV can be combined to give

$$\beta_0'=\beta'/[1+(m\varepsilon)^{1/2}/(6\pi\eta a^2)] \qquad \text{(V)}$$

The expression for β' is obtained in a similar way:

$$\beta'=1/[1+(mkT)^{1/2}/(2\sqrt{6}\,\pi\eta a^2)] \qquad \text{(VI)}$$

If ϕ is the quantum yield, β_0' is equal to $1-\phi$. Hence, the quantum yield can be calculated when ε and η are given.

In the photolysis of azomethane, $2a$ in Eq. IV should be replaced by $2s_0$, the distance between the two carbon atoms in an azomethane molecule. Consequently, Eq. V should be written as

$$\beta_0'=a\beta'/s_0[1+(m\varepsilon)^{1/2}/(6\pi\eta a s_0)] \qquad \text{(VII)}$$

One of the uncertainties in this case is the magnitude of a, the effective radius of a free methyl radical. Another uncertainty, which

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5) Reported values of diffusion energy for free radicals in solution are meagre: Polystyrene radicals (in benzene), 1.9 kcal./mol. (G. M. Burnett, *Trans. Faraday Soc.*, **46**, 772 (1950)); polymethylmethacrylate radicals (in methylmethacrylate), 2.8 kcal./mol. (M. S. Matheson et al., *J. Am. Chem. Soc.*, **71**, 497 (1949); ibid., **73**, 1700 (1951)).

6) a) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); b) *J. Am. Chem. Soc.*, **77**, 2042 (1955); c) ibid., **78**, 5486 (1956); d) *Z. Elektrochem.*, **64**, 153 (1960).

gives more difficulty in the evaluation of β_0' is the value of ε. Although an energy of 56 kcal./mol.[1] is liberated in the photolysis with 366 mμ, the share for the methyl radicals is unknown. Moreover, two methyl radicals will not always separate in opposite directions.

On account of these uncertainties, it seems impossible to compute β_0' by Eq. VII in this case. However, approximate values of β' may be estimated, since it has no relation to ε, and, as a first approximation, a may be regarded as equal to s_0, which is known to be 1.80 Å from its molecular structure[7,8]. As seen in Table IV, β' thus calculated is almost unity at low temperatures. It decreases with a rise in temperature, but is still greater than 0.9 at the highest temperature for all the solvents. If, therefore, β' in Eq. VII is put equal to unity,

$$1/\beta_0' = (s_0/a) + (m\varepsilon)^{1/2}/(6\pi a^2)\cdot 1/\eta \qquad \text{(VIII)}$$

Since β_0' is equal to the yield of ethane found by experiment, there should be a linear relationship between the ratio N_2/C_2H_6 and the reciprocal viscosity, if Eq. VIII is applicable.

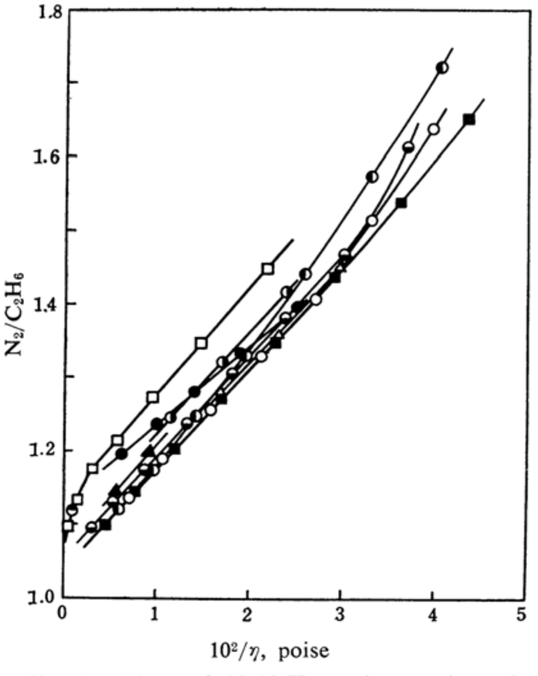

Fig. 3. Plots of N_2/C_2H_6 against reciprocal viscosity. ○, *n*-Hexane; ◐, *n*-Octane; ◑, Cyclohexane; ◒, Toluene; ◓, *tert*-Amyl alcohol; ●, Styrene; △, Benzene; ▲, *o*-Xylene; □, Ethanol; ■, Ethyl acetate

Figure 3 shows that Eq. VIII represents experimental results rather satisfactorily. At high viscosities or at low temperatures, where the equation is expected to be applicable, most plots are linear, run parallel and nearly coincide with each other. The plots for *n*-hexane, *n*-octane and ethyl acetate give identical intercepts on the ordinate, from which a is obtained as 1.73 Å, in approximate agreement with the 1.80 Å assumed above to estimate β'. These plots have almost the same slope at high viscosities, from which ε is obtained as 33.8 kcal./mol. This appears to be not an unreasonable value for the virtual energy separating two methyl radicals in opposite directions to a distance, s_t, in view of the total energy of 56 kcal./mol. liberated in the photolysis. By inserting this ε value into Eq. IV, the distance of initial separation, s_t, is calculated. The values obtained for *n*-hexane, for example, are shown in Table V. These s_t values also appear to be not unreasonable.

TABLE V. s_t VALUES FOR *n*-HEXANE

Temperature °C	s_t Å	$s_t - 2s_0$ Å
−75	3.93	0.33
0	4.59	0.99
75	5.46	1.86

Figure 3 shows however a general tendency, at low viscosities or at high temperatures, for deviation from the linear plot to appear in the direction of yielding less ethane than would be expected from Eq. VIII. A part of the deviation may be ascribed to the factor β' in Eq. VII, since β' becomes smaller with a rise in temperature, as is shown in Table IV. This effect is, however, by far too small to explain the observed deviations. The deviations seem, therefore, to indicate that the effect of the molecular structure of the medium, which was neglected in the theory, has to be taken into account. A simlar indication has been obtained by Noyes and his coworkers in the photolysis of iodine[6d,9]. As was cited by them in their papers, "Rabinowitch's cage"[10] originated from the idea that if two atoms are separated by only a small distance, the surrounding solvent molecules tend to force the atoms toward each other, while, if the atoms are separated sufficiently enough so that solvent molecules can squeeze between them, solvent molecules will force the atoms farther apart. If, in the present work, the distance of initial separation for a pair of methyl radicals is largely controlled

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[7] According to H. Boersch (*Sitzungsber. Akad. Wiss. Wien.*, **144**, 1 (1935)), azomethane is of the trans form, with C-N=1.47, N-N=1.24 Å and ∠CNN=110°. s_0 is therefore obtained as 1.80 Å.

[8] L. Pauling estimates the van der Waals radius of a methyl radical in a molecule as 2.0 Å. ("The Nature of the Chemical Bond", Third Ed., p. 261. Cornell Univ. Press, Ithaca, N. Y. (1960)).

[9] D. Booth and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1868 (1960); L. F. Meadows and R. M. Noyes, ibid., **82**, 1872 (1960).

[10] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.* **32**, 547 (1936).

by the viscosity of the medium, it may be expected from the above behavior of solvent molecules that the experimental yield of ethane will be higher at high viscosities but lower at low viscosities than that predicted by Eq. VII, and that it will approximately conform to the equation in an intermediate range of viscosity. Figure 3 appears to be in general agreement with such an expectation, though the deviation from the linear plot to give a higher yield of ethane is not seen in the range of viscosity studied here except for ethanol.

The plots for the various solvents in Fig. 3 do not completely coincide with each other, which indicates that viscosity is not the only controlling factor. It is probably necessary, for a better description of the matter, to take account of the structure and specific nature of the individual molecules of the solvent. The smaller slope of the plot for styrene seems, however, to have resulted from its polymerization, which has been found to be induced by the photolysis(3). Since the polymerization increases with the temperature, the viscosity of the medium probably becomes higher than in pure styrene at high temperatures.

Summary

Experimental results for the cage combination of methyl radicals, obtained by the photolysis of azomethane in various solvents, have been discussed with reference to the effects of solvent and temperature. An attempt to interpret the results by treating both the cage combination and the escape of methyl radical from the cage as though they were elementary processes has been found to be not very successful, probably owing to the over-simplification involved in such a treatment. Another attempt to apply Noyes's theory, that assumes diffusion in the viscous continuum, has been found to be rather satisfactory. However, a comparison of the theory with the experimental results indicates that the molecular structure of the medium, as well as the structure and property of individual molecules of the solvent, need to be taken into account for a better description of the matter.

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