

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1964, by the American Chemical Society

VOLUME 86, NUMBER 10

MAY 20, 1964

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., PROCESS RESEARCH DIVISION, LINDEN, N. J.]

The Cage Effect in Solution and Gas Phase with Application to the Determination of Rate Constants

BY RICHARD K. LYON

RECEIVED JUNE 18, 1963

The hitherto not generally recognized gas phase cage effect has been demonstrated. The Samuel-Magee model¹ permits calculation of the recombination rate constant of methyl radicals from the observed efficiencies of the gas phase cage effect. The rate constant thus calculated agrees well with that measured by Gomer and Kistiakowsky.² The application of this theory to investigations of the cage effect in solution gives generally satisfactory agreement. It is concluded that the model provides a general method for obtaining rate constants from measurements of the efficiency of the cage effect.

Introduction and Definitions

The fact that radicals can react with each other very rapidly and that they are necessarily created and destroyed in pairs produces two well known effects in solution chemistry: the diffusion controlled reaction and its obverse, the cage effect.^{3,4} The rate of the reaction $A + B \rightarrow AB$ is given by

$$d[AB]/dt = \int k_R[A][B]dV/V = k_R\overline{[A][B]} \quad (1)$$

where $\overline{[A][B]}$ is read as the product of the local concentrations of A and B averaged over the entire volume of the solution. If A and B are formed from the same molecule (for example, by the reaction $ANNB \rightarrow A + B + N_2$) then $\overline{[A][B]} \gg \overline{[A]} \times \overline{[B]}$ for newly formed radical pairs. But $\overline{[A][B]} \ll \overline{[A]} \times \overline{[B]}$ for old radicals, because a radical in the vicinity of another radical probably will not live to old age. If k_R is high enough, the rate-determining step in destroying the old radicals will be the diffusion of the radicals toward each other, and the observed rate constant will be

$$k_T = 4\pi\rho DL \quad (2)$$

where D is the diffusion coefficient of the radicals, ρ is the encounter diameter, and L is the Avogadro number. This is a well known equation for a diffusion controlled reaction.

We may write $d[AB]/dt$ as the sum of two terms; the reactions of old radicals and of new radicals, *i.e.*, the diffusion controlled reaction and the cage effect.

$$d[AB]/dt = k_T\overline{[A]} \times \overline{[B]} + \frac{1}{2}(1 - F)I \quad (3)$$

where I is the rate of radical generation and F is the

(1) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

(2) R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951), also see A. Sheep, *ibid.*, **24**, 939 (1956).

(3) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(4) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950), and the following papers.

probability that a new radical pair will diffuse apart to the average distance between radicals instead of react with each other. If the rate constants of A and B for reaction with solvent are so large that $k_{AS}k_{BS} \cdot (S)^2 \gg 2Ik_R$, then the steady-state concentrations of A and B in the bulk will be so small that no significant amount of AB can be produced by bulk recombination. In such reactive solvents AB can only be formed by cage effect recombination.

In the experiments to be reported here CH_3NNCH_3 has been photodecomposed in high density propane gas (0.087 to 0.260 g./cc. at 98°). By variation of the density, the diffusion coefficient can be changed and the variation of the cage effect efficiency is observed. It should be remembered that at these high gas densities the diffusion coefficient is not much larger than in solution so that the existence of a cage effect is not surprising.⁵

Experimental

Azomethane was purchased from Merck of Canada and was proved pure by gas chromatography. The propane used was Matheson research grade. Because the amount of propane used was very large compared to the amount of ethane formed during the reaction, it was necessary to correct the observed ethane for a trace of ethane present as an impurity in the propane. Aside from this, the propane was pure.

The amounts of azomethane and propane to be used were measured by filling calibrated volumes to measured pressures and condensing the material into the reactor with liquid N_2 . The azomethane concentration was 2 to 3%. The photolysis itself was done in a conventional thermostat using a medium pressure Hanovia Hg lamp with a filter to remove radiation below 2800 Å. The photolysis usually was run to about 25% decomposition of the azomethane. These experimentally necessary high conversions are justifiable in view of the large excess of propane present and the fact that the products are much less susceptible to methyl radical attack than is propane. Following a run, the entire sample was injected into a gas chromatograph. Using a silica gel column,

(5) Diffusion controlled reaction is well established in the high pressure gas phase recombination of ions. See J. Sayers, "Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press, Inc., New York, N. Y., 1962, Chapter 8.

N_2 , NO, CH_4 , C_2H_6 , and C_3H_8 were all very well resolved. The sensitivity of the instrument to each substance was determined with the pure substance.

The only point in the experiment which caused any difficulty was the reactor. It had to be transparent to ultraviolet light, withstand pressures up to 50 atm. at 98°, hold good vacuum, and have a small dead volume. The problem was solved by attaching a 5-mm. i.d. Pyrex to quartz graded seal to a Fisher Porter glass needle valve. The reactor was 12.5 cm. long with a dead volume of 20%. The weak point of the apparatus was the graded seal; but if properly annealed, the reactors seldom exploded in the pressure range covered.

Results and Their Theoretical Analysis

The observed C_2H_6/CH_4 ratios are reported in Table I. If ethane formation were in competition with methane formation by abstraction from propane, the ratio should decrease with increasing propane density whereas it is observed to increase. In a separate set of experiments, 1% of NO was added to the reaction mixture. The ratio C_2H_6/N_2 was not significantly changed (0.065 ± 0.024 as compared to 0.044 in the uninhibited case), but the ratio CH_4/C_2H_6 decreased by a factor of three. Therefore, when an ethane molecule is formed it is formed directly from the photodecomposed azomethane.

TABLE I

No. of expt.	d , g./cc.	D , cm. ² /sec.	C_2H_6/CH_4	k_R , cc./mole sec.
Methyl Radical Recombination				
Propane at 98°				
2	0.087	4.96×10^{-3}	0.063 ± 0.011	17×10^{13}
2	.177	2.33×10^{-3}	$.078 \pm .012$	8.3×10^{13}
3	.200	1.93×10^{-3}	$.089 \pm .008$	7.5×10^{13}
2	.260	1.86×10^{-3}	$.10 \pm .011$	8.2×10^{13}
			Av.	10.2×10^{13}
			Av. spin corrected	2.6×10^{13}
Isooctane at 25° (ref. 11)				
0.688		7.85×10^{-5}	1.70	7.4×10^{13}
			Spin corrected	1.8×10^{13}
Low pressure gas phase random combination (ref. 2)				
				2.2×10^{13}
Ethyl Radical Recombination				
Isooctane at 25° (ref. 19)				
0.688		5.82×10^{-5}		1.87×10^{13}
			Spin corrected	0.47×10^{13}
Low pressure gas phase random recombination at 25° (ref. 18)				
				0.5×10^{13}

Recently Rebbert and Ausloos⁶ have proved that azomethane photolysis occurs by two mechanisms: $CH_3N_2CH_3 + h\nu \rightarrow 2CH_3 + N_2$ or $C_2H_6 + N_2$. The efficiency of the second process is less than 1% that of the first, but increases with increasing pressure and increasing wave length. The pressure dependence is less than linear and appears to approach a high pressure limit; for 3660 Å. light the efficiency of the second process at 66.5, 127.7, and 246.5 mm. is, respectively, 0.37, 0.66, and 0.69%. Since the efficiency of ethane production in the present experiments is much higher (17% at 0.26 g./cc.), it is to be attributed to the cage effect. Rebbert and Ausloos argue to this conclusion for their observed ethane production in the liquid phase.

In order to interpret our results it is necessary to assume a model, and for this purpose the Samuel-Magee model¹ will be used. In this model, as applied

to our case, it is assumed that the yield of ethane is given by eq. 4

$$C_2H_6 = \int_0^\infty \int_0^\infty k_R [CH_3]^2 4\pi r^2 dr dt \quad (4)$$

while the distribution of methyl radicals throughout all space and time is given by the usual equation for competition between diffusion and chemical reaction, eq. 5, and by the boundary condition, eq. 6.

$$\frac{\partial [CH_3]}{\partial t} = D\nabla^2 [CH_3] - 2k_R [CH_3]^2 - k_A [CH_3][C_2H_6] \quad (5)$$

$$[CH_3]_{t=0} = (N_0/\pi^{3/2}b^3) \exp(-r^2/b^2) \quad (6)$$

In the above expressions, N_0 is the number of methyl radicals initially formed by the photolysis (*i.e.*, 2), b is discussed later, and the other quantities have their usual significance.

The reader may be puzzled by the use of the idea of concentration since there are only two methyl radicals. In the above expressions, the concentration of methyl radicals merely means the probability density of methyl radicals. This meaning of concentration may seem unusual, but it is the only valid meaning in writing a chemical rate expression. When concentration means bulk concentration, and not probability density (as is the case in a diffusion controlled reaction), the rate expression characterizes the diffusion process and has little connection with the chemical reaction itself.

Equation 5 assumes that the macroscopic long time diffusion law (Fick's law) is valid for the short times and distances (10^{-11} to 10^{-8} sec. and 4 to 400 Å.) involved in the cage effect. Kirkwood^{7,8} has advanced arguments that the Fick's law is valid in solution at all times longer than 10^{-13} sec.

Equation 5 is not analytically soluble,⁹ but numerical solutions have been published.¹⁰ These solutions give C_2H_6/CH_4 as a function of two reduced parameters, B and E , where $B = b^2 k_A [C_3H_8]/4D$ and $E = k_R N_0/\pi^{3/2} b D$.

If one is to compare theory and experiment, it is necessary to estimate b and D . The initial distribution of methyl radicals is defined by b ; effectively b is the radius of the volume in which the methyl radicals are initially formed. The simplest and most reasonable assumption is that this volume is volume occupied by the azomethane molecule before it was decomposed. Hence, $4/3\pi b^3 = MW/\rho L$ where $MW/\rho L$ is the number density of the solvent molecules.

Two possible objections may be raised to this procedure: if the fragments from photolysis are formed with large excess kinetic energy, they might travel some distance before the viscous drag of the solution slows them down; alternatively, if the azomethane molecule initially decomposes to a CH_3 and a CH_3N_2 radical, these may separate some distance by diffusion

(7) J. G. Kirkwood, *J. Chem. Phys.*, **14**, 180 (1946).

(8) J. G. Kirkwood, F. P. Buff, and M. S. Green, *ibid.*, **17**, 988 (1949).

(9) This equation neglects the fact that as the radicals diffuse apart their positions will tend to become correlated, due to reaction with each other. This second-order effect has no significant influence on the present work, but is doubtless important in systems where the diffusion constant is very low, especially low temperature matrix isolation experiments. Therefore, the statement in Table 11 that as E becomes infinite, the fraction of radicals escaping becomes zero, is simply a statement of the properties of equations and not a description of reality.

(10) D. A. Flanders and H. Fricke, *J. Chem. Phys.*, **28**, 1126 (1958).

(6) R. E. Rebbert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962).

before the $\text{CH}_3\text{N}_2\cdot$ decomposes and ethane formation can begin. Szwarc and co-workers¹¹ have demonstrated that the caged formation of ethane by photolysis of azomethane in isooctane solution is the same within experimental error for light of 2537 and of 3600 Å. Hence, the excess energy of the photodecomposition does not go into kinetic energy, and the first objection is excluded. The second objection assumes that the radical $\text{CH}_3\text{N}_2\cdot$ exists and there is no evidence for the existence of any radical of the type $\text{RN}_2\cdot$. Further, it is to be remembered that the thermal decomposition of azomethane proceeds with a pre-exponential of $10^{15.7}$ sec.⁻¹ while vibrational frequencies are of the order of 10^{13} . Various theorists¹² have explained this and other seeming anomalies by assuming that both CN bonds break simultaneously. If one interprets the pre-exponential in terms of an entropy of activation, this assumption produces a more disordered activated complex and hence explains the high pre-exponential.

It must also be noted that for a sequential reaction, $\text{CH}_3\text{NNCH}_3 \rightarrow \text{CH}_3\text{NN} + \text{CH}_3$ (slow and rate determining), $\text{CH}_3\text{NN} \rightarrow \text{CH}_3 + \text{N}_2$ (fast), the reverse step of the rate-determining step is a radical-radical recombination. Such recombinations occur with little or no activation energy, hence the rate-determining step has an activation energy less the net endothermicity by the strength of the $\text{CH}_3\text{-NN}$ bond. In fact, the activation energy is 53 kcal. and the endothermicity only 16 kcal.¹³ A bond with a negative strength of 37 kcal. seems unreasonable so that one must conclude that the reaction is not sequential.

To estimate D for the $\text{CH}_3, \text{C}_3\text{H}_8$ pair one must obtain the diffusion coefficient under ideal conditions and the correction factor for the very nonideal conditions used. Because of its extreme chemical reactivity, very little is known about the physical properties of the methyl radical; however, it is comparatively easy to calculate the diffusion coefficient of the $\text{NH}_3, \text{C}_3\text{H}_8$ pair using the procedure given by Hirschfelder, Curtiss, and Bird.¹⁴ Using this procedure, $D_{\text{CH}_3, \text{C}_3\text{H}_8}$ is estimated to be $0.356 \text{ cm}^2/\text{sec.}$ at 1 atm. and 98° . This simple analogy is by no means exact, since the interaction forces between NH_3 and C_3H_8 are different from the forces between CH_3 and C_3H_8 . However, since the diffusion coefficient is not hypersensitive to the forces, this is an acceptable first approximation.

It has been demonstrated^{14,15} that the law of corresponding states provides good estimates of the non-ideality corrections of diffusion coefficients, especially for nonpolar mixtures. Using the PVT data of Deschner and Brown¹⁶ the diffusion coefficients given in Table I were calculated by the method of Slattery and Bird.¹⁶

In the discussion of cage effect measurements made in liquid solutions of saturated hydrocarbons, a much more direct procedure is possible. Rosman and Noyes¹⁷

have measured $D_{\text{I}, \text{C}_3\text{H}_8}$ as the rate constant at 25° of the diffusion controlled reaction. The value given in Table I for $D_{\text{CH}_3, \text{C}_3\text{H}_8}$ is $D_{\text{I}, \text{C}_3\text{H}_8}$, multiplied by $\sqrt{\mu_{\text{I}, \text{C}_3\text{H}_8} / \mu_{\text{CH}_3, \text{C}_3\text{H}_8}}$. This neglects the fact that CH_3 and I are not the same size, but in both cases the hydrocarbon contributes most of the mean diameter for the colliding pair. Hence, this is not a large error.

Using the above procedures, one may calculate the value of B , since the rate of reaction between CH_3 and C_3H_8 is known.¹⁸ At 0.087 g. of propane per cc. and 98° , B is about 10^{-10} . Flanders and Fricke¹⁰ found that for values of $B < 10^{-4}$ the product ratio ($\text{C}_2\text{H}_6/\text{CH}_4$) was within 1-2% of the $B = 0$ value. Physically this is saying that hydrogen abstraction from propane by methyl radical is much too slow a process to compete with the diffusion of methyl radical. In general, only very fast radical scavengers can produce measurable effects on the efficiency of the cage effect.

Hence, the observed product ratio is a function of only one reduced variable, $E = k_R N_0 / \pi^{3/2} b D$. In Table II the numerical results of Flanders and Fricke

TABLE II
EFFICIENCY OF THE CAGE EFFECT (AFTER FLANDERS AND FRICKE¹⁰)

$F = 1 -$								
$E/2\sqrt{2}$	0.851	0.666	0.551	0.449	0.269	0.153	0.00	
$E = k_R N_0 /$								
$\pi^{3/2} b D =$								
0	0.515	1.544	2.50	4.12	10.30	25.74	∞	

at $B = 0$ are listed. F is the probability that the radicals will escape the cage and is directly related to the product ratio ($F = \text{CH}_4/\text{CH}_4 + 2\text{C}_2\text{H}_6$). $F = 0$ at $E = \infty$ and $F - 1 = E/2\sqrt{2}$ as $E \rightarrow 0$; hence for inefficient cages a plot of $F - 1$ against E and for efficient cages a plot of F against $1/E$ are useful in determining E from an observed value of cage efficiency.

Discussion

CH_3 .—Using the procedures described above, the values of k_R given in Table I are calculated from our observed $\text{C}_2\text{H}_6/\text{CH}_4$. Szwarc¹¹ has measured this ratio for the photolysis of CH_3NNCH_3 in isooctane at 25° . This gives a value of k_R in good agreement with the present determination.

Gomer and Kistiakowsky² determined k_R for the low pressure gas phase random recombination of methyl radicals to be 2.2×10^{13} cc./mole sec. In these experiments, the electron spins of a colliding pair of radicals are randomly oriented so that of four collisions three lead to a triplet state and one yields a singlet. Presumably, ethane has no bonding triplet states, and spin conservation is strictly obeyed by light particles. Hence, only the singlet collision is effective. However, in the cage effect experiments on the recombination, radicals are formed from the same singlet molecule and react with each other in less than 10^{-9} sec. Again, spin must be conserved so that to compare cage results with random recombination rates, a correction factor of four is necessary.

C_2H_5 .—The efficiency of the cage effect in the photolysis of azoethane has also been determined by Szwarc

(11) L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

(12) C. Steel and K. J. Laidler, *J. Chem. Phys.*, **34**, 1827 (1961).

(13) G. Chiltz, C. F. Aten, Jr., and S. H. Bauer, *J. Phys. Chem.*, **66**, 1426 (1962).

(14) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 600-602.

(15) J. C. Slattery and R. B. Bird, *Am. Inst. Chem. Eng. J.*, **4**, 137 (1958).

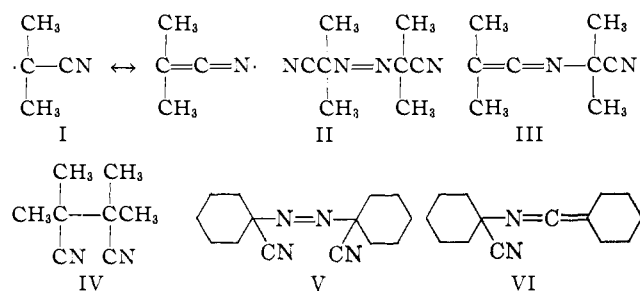
(16) W. W. Deschner and G. G. Brown, *Ind. Eng. Chem.*, **32**, 836 (1940).

(17) H. Rosman and R. M. Noyes, *J. Am. Chem. Soc.*, **80**, 2410 (1958).

(18) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Pergamon Press, London, 1961.

and co-workers.¹⁹ From their value at 25° the value of $k_{R,Et}$ given in Table I is readily calculated assuming $D_{Et,C_6H_{18}} = D_{I,C_6H_{14}} \sqrt{\mu_{I,C_6H_{14}}/\mu_{Et,C_6H_{18}}}$ and $k_{D,Et}/k_{R,Et} = 0.16$. The cage effect value of $k_{R,Et}$ compares favorably with the value given by Kerr and Trotman-Dickenson ($\log k_{R,Et} = 14.2 - (2000 \pm 1000/2.3 RT)$).¹⁸

(CH_3)₂CCN.—In the present theory it is assumed that the radicals are randomly distributed throughout the available volume (the reciprocal number density). No allowance has been made for the effect of structure of the radical generating molecule. This is justifiable only as an approximation, and the work of Hammond and co-workers^{20,21} on the cyanopropyl radical (I) provides a test of this approximation.



The cyanopropyl radical can be generated from either azoisobutyronitrile (II) or from dimethyl-N-(2-cyano-2-propyl)ketenimine (III). The radicals either diffuse apart or react to form tetramethylsuccinonitrile (IV) (and some III). In CCl₄ at 62.5° Hammond reports an efficiency of radical generation of $a = 0.46$ for II but $a = 0.35$ for III. In a similar set of experiments with azocyanocyclohexane (V) and N-(1-cyanocyclohexyl)ketenimine pentamethylene (VI) the values $a = 0.67$ and $a = 0.42$, respectively, were found. It seems very likely that the difference in efficiencies is due to a difference in spatial distribution at the moment of radical formation. Although these effects are real, they are not large.

CH₃Hg.—Derbyshire and Steacie²² have studied the photolysis of CH₃HgCH₃ in *n*-hexane solution. At 25°, they report C₂H₆/CH₄ = 0.204 ± 0.016 independent of light intensity and CH₃HgCH₃ concentration. The authors attempt to explain the result in terms of an initial excitation of the methyl radicals. The excited radicals can abstract hydrogen from hexane or be deactivated. The deactivated radicals are assumed to react with hexane so slowly (due to the activation energy for this process), that nearly all of them recombine. Since the ethane/methane ratio is then determined by competition between abstraction and deactivation, the observed first-order rate for ethane production is explained.

However, using known rate constants¹⁸ one can readily calculate that under Derbyshire and Steacie's conditions, the steady-state concentration of CH₃ is so low that ethane formation by random recombination is negligible and methane should be the only product. Since ethane rather than methane is pro-

duced in excess of expectation, the logical explanation is the cage effect.²³

The C₂H₆/CH₄ ratio is small compared to that for CH₃NNCH₃ photolysis. This is presumably due to the transient existence of CH₃Hg. The pyrolysis of CH₃HgCH₃ proceeds with a normal frequency factor ($A = 2 \times 10^{13}$ sec.⁻¹) and an activation energy 6 kcal. less than the endothermicity of the reaction CH₃HgCH₃ → 2CH₃ + Hg.²⁵⁻²⁷ Gowenlock, Polanyi, and Warhurst interpret this to mean that the reaction is CH₃HgCH₃ → CH₃ + CH₃Hg (rate determining) followed by CH₃Hg → Hg + CH₃. They conclude that $D(Hg - CH_3) = 6 \pm 2$ kcal. There is some other chemical evidence for the existence of HgCH₃ as a short-lived intermediate,²⁸ and some analogous substances are known, for example HgH.²⁹ Therefore, it is reasonable to assume that it occurs during CH₃HgCH₃ photolysis reducing caged ethane formation.

Using the formula in footnote 30 one finds $k_2 = 5 \times 10^8$ sec.⁻¹. If the frequency factor for CH₃Hg decomposition is the same as for CH₃HgCH₃, the activation energy for the CH₃Hg decomposition is about 4.8 kcal. (compare 6 ± 2 kcal.).

The activation energy for self-diffusion in *n*-hexane may be calculated from the temperature dependence of the viscosity³¹ to be 1.7 kcal. If the activation energies for diffusion of CH₃ and CH₃Hg are about the same as the activation energy of self-diffusion, they will approximately ($1/2 \times 4.8 - 3/2 \times 1.7$) cancel the activation energy for CH₃Hg decomposition. Hence the ethane quantum yield should be approximately temperature independent. However, the authors admit that their solvent may contain traces of olefins, and as the temperature is decreased these become increasingly effective scavengers for free methyl radicals, since the activation energy for reaction of methyl with olefin is much less than that with *n*-hexane. The methane yield may, therefore, decrease with temperature.

This is exactly what Derbyshire and Steacie report. Ethane quantum yield is constant between 25 and -80° within 8%, while methane quantum yield drops by a factor of three.

Conclusions

1. The agreement between directly measured rate constants and activation energies and those estimated from the cage effect is good. Although this may,

(23) This interpretation is considerably strengthened by the observations of Rebbert and Ausloos²⁴ on the photolysis of dimethylmercury. They report $CH_3CD_3/C_2H_6^{1/2}C_2D_6^{1/2} = 0.138$ for a solid solution of CH₃HgCH₃ + C₂D₆HgC₂D₆ in C₂H₅OH at 77°K.

(24) R. E. Rebbert and P. Ausloos, "Fifth International Symposium on Free Radicals," 1961, Upsala, Gordon and Breach, New York, N. Y.

(25) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 269 (1953).

(26) C. M. Laurie and L. H. Long, *Trans. Faraday Soc.*, **51**, 655 (1955).

(27) T. L. Cottrell, "The Strength of Chemical Bonds," Butterworths, London, 1958, pp. 209 and 210.

(28) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

(29) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1959.

(30) Consider the sequential process $AXA \xrightarrow{k_1} A + AX, AX \xrightarrow{k_2} A + X$ where the lifetime of AX is large compared to D/b^2 . In this case the cage will be so inefficient that $F \approx 1 - (E/2\sqrt{2})$ and $E = k_R N_0 / \pi^{3/2} D_{AB} b'$ where $b' = \sqrt{\frac{2(D_A + D_{AX})}{k_2}}$.

(31) Calculated from the data in "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(19) M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Szwarc, *Proc. Chem. Soc.*, 304 (1962).

(20) C. S. Wu, G. S. Hammond, and J. M. Wright, *J. Am. Chem. Soc.*, **82**, 5386 (1960).

(21) G. S. Hammond, *et al.*, *ibid.*, **82**, 5394 (1960).

(22) D. H. Derbyshire and E. W. R. Steacie, *Can. J. Chem.*, **32**, 457 (1954).

in part, be fortuitous, and other methods are certainly more accurate, the new method has value in that it can easily be applied to systems where other methods are difficult if not impossible to use. 2. Conversely, quantitative estimation of cage effect efficiency is possible. Even in systems in which k_R and D can be estimated only within wide limits, it is possible to decide whether or not the cage effect is an order of magnitude large enough to be important. 3. Since the Samuel-Magee model works in a comparatively simple chemical system, its extension to the more complex systems of radiation chemistry becomes

more confident. 4. The technique of varying the density at constant temperature in the vicinity of the critical region provides a method of changing the initial distribution of radicals and their diffusion coefficients. This should prove useful in characterizing radiation chemistry systems.

Acknowledgments.—The author wishes to acknowledge with gratitude the assistance of Mr. Roger Parry in doing the experimental work presented herein and the helpful discussions he has had with Dr. William Bartok. He also wishes to thank the Esso Research and Engineering Co. for permission to publish this article.

[CONTRIBUTION NO. 3022 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Cage Effects in Thermal Decomposition Reactions in Solution

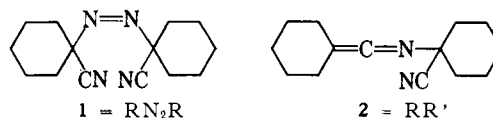
BY HAROLD P. WAITS AND GEORGE S. HAMMOND

RECEIVED SEPTEMBER 10, 1963

Decomposition of an azonitrile (azo-1-cyanocyclohexane) and the related ketenimine (N-(1-cyanocyclohexyl)pentamethyleneketeneimine) has been carried out in solutions containing varying amounts of reactive scavengers. In both cases 1,1'-dicyanobicyclohexyl is a principal product of geminate recombination. Decrease in the yield of this product at high scavenger concentrations is taken as a measure of the interference, by scavenger, with geminate recombination. Both the concentration level ($\sim 0.1 M$) at which scavenging of caged pairs begins and the functional form of the dependence of the effect on scavenger concentration show significant deviation from quantitative predictions of approximate theories which emphasize the importance of secondary recombination. An alternative approximate model which emphasizes interference with primary recombination by scavengers which are nearest neighbors at the time of decomposition is developed.

A significant source of contrast between dissociative reactions in liquid solution and in the gas phase arises from the fact that in liquid media collisions occur in sets. Consequently, a pair of reactive fragments produced by either homolytic or heterolytic fission in solution may undergo *geminate recombination* while they are still close neighbors. Since the phenomenon was first discussed by Franck and Rabinowitch,¹ the theory of the "cage effect" has been discussed by a number of authors.²⁻⁴ Emphasis in theoretical treatments has been placed on analysis of the part of the process referred to by Noyes^{2b} as *secondary recombination*. Secondary recombination is the sum of all recombinations that occur as a consequence of re-encounters between pairs which have at some time been separated by one or more diffusive displacements. All treatments predict two important characteristics of the interference by scavengers with secondary recombination: (1) the effect should become measurable at scavenger concentrations of the order of $10^{-2} M$ or lower; (2) the fractional decrease of the amount of secondary recombination should be a linear function of the square root of the concentration of scavenger. It is also predicted^{2b} that, even after secondary recombination has been eliminated, there will be a residual cage effect attributable to *primary recombination*, i.e., recombination of pairs before they have moved from the positions that they occupy immediately after bond breaking.

Good evidence for the reality of the cage effect has been produced in the study of radical-producing decomposition reactions effected thermally, photochemically, and by high energy radiation.^{3,5-10} A common method of demonstration is to show that addition of scavenger in low concentration reduces the yields of coupling products to a level that remains constant over a considerable range of larger scavenger concentrations. Although a number of the reports include quantitative treatments which seem to support^{3,6,11} the theory based on extensive secondary recombination, none of the studies have involved variation of the concentration of highly reactive scavengers at high scavenger concentrations. We undertook such experiments in the hope of characterizing both primary and secondary recombination. Choice of a thermal decomposition reaction, rather than photolysis, for the study was dictated by our belief that the action of scavengers in thermolysis is less complicated. The radical sources chosen were 1,1'-azocyanocyclohexane (1) and the related ketenimine 2.



- (1) T. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).
 (2) (a) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); (b) *J. Am. Chem. Soc.*, **77**, 2042 (1955); (c) **78**, 5486 (1956); (d) *J. Phys. Chem.*, **65**, 763 (1961); (e) "Progress in Reaction Kinetics," G. Porter, Ed., Pergamon Press, London, 1961.
 (3) J. C. Roy, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **76**, 3274 (1954).
 (4) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

- (5) A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 3486 (1955).
 (6) F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).
 (7) (a) G. S. Hammond, *et al.*, *ibid.*, **77**, 3244 (1955); (b) **81**, 4876, 4878 (1959); (c) **82**, 5386, 5394 (1960); (d) **85**, 1501 (1963).
 (8) R. K. Lyon and D. H. Levy, *ibid.*, **83**, 4290 (1961).
 (9) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 543 ff.
 (10) G. S. Hammond and J. R. Fox, *J. Am. Chem. Soc.*, **86**, 1918 (1964).
 (11) (a) J. Jortner, *et al.*, *J. Phys. Chem.*, **65**, 1232 (1961); (b) **66**, 2039 (1962).