The Raman spectra were recorded photographically on a grating instrument constructed in this laboratory. A Spectra-Physics Model 125 He–Ne laser was used for the excitation source, and the use of a Spectra-Physics Model 310 polarization rotator made the identification of the polarized lines a straightforward matter. By using a Corning filter, No. SPO-98565, in front of the slit, it was possible to obtain Raman spectra above 200 $\mathrm{cm^{-1}}$ from the exciting line, although the maximum transmission of the Corning filter is not reached until 400 $\mathrm{cm^{-1}}$. Several Rowland ghosts appear in the region between 200 and 400 $\mathrm{cm^{-1}}$ but they are weak and do not interfere. On the other hand, the region below 200 $\mathrm{cm^{-1}}$ is heavily populated with ghosts. A special Baird filter permitted one to obtain high transmission from about 40 to 200 $\mathrm{cm^{-1}}$ while removing all the ghosts. However, the constant presence of lines at 63 and 91 $\mathrm{cm^{-1}}$ was observed.

Acknowledgment. This work was supported by the Advanced Research Projects Agency through the Purdue IDL program. We are indebted to Dr. John Ferraro and Dr. Clarence Postmus of Argonne National Laboratories for making the high-pressure facilities available to us and helping with the measurements, to Dr. Stanley Abramowitz of the National Bureau of Standards for supplying a sample of ^{6}LiOH, to Dr. V. Thornton of Phillips Petroleum Company for the polyethylene used for the far-infrared cells, and to Mr. Jim Saunders, Mr. Jack Fisher, and Mr. Arthur Curry for experimental help in this laboratory.

The Microscopic Mechanism for Diffusion and the Rates of Diffusion-Controlled Reactions in Simple Liquid Solvents[1]

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Received September 15, 1969

Abstract: Standard theoretical treatments of chemical reaction kinetics generally neglect any mean interaction potentials or "excluded volume" effects that might interfere with the relative diffusion of a pair of reactant molecules in solution. Analyses of the computer-generated simulation data for a model dense fluid of Lennard-Jones disks have shown that the microscopic mechanism for diffusion in simple liquids is largely "cooperative" in nature, and that short-range correlations associated with this cooperative mechanism tend to slow the relative diffusion of pairs of molecules approaching to within three–four diameters of each other. In this paper we examine the impact of these results upon the theoretical prediction of diffusion-controlled reaction rates and the physical interpretation of several other very fast chemical processes in solution.

The use of diffusion models to treat the kinetics of fast reactions in solution was first proposed by Smoluchowski[3] and has more recently been reviewed by Noyes.[4] Although this approach is widely used and frequently provides satisfactory order-of-magnitude predictions of rate constants, several fundamental difficulties remain. These difficulties appear to stem primarily from a lack of detailed information regarding the microscopic mechanism for diffusion in liquids. In particular, the manner in which this mechanism might affect the *relative* motions of molecules in a liquid is not well understood.

In Smoluchowski-type treatments of chemical reaction kinetics, it is frequently assumed that the relative diffusion of molecules of two reactant species is described by a coefficient that is just the sum of the bulk diffusion coefficients for the two species in solution. This assumption is equivalent to a supposition that no correlation exists between the time-dependent relative displacements of two solute molecules and their relative positions and motions at previous times. It is not altogether clear that this supposition is valid for molecules that are separated by only short distances, and indeed a deviating behavior—the so-called "solvent cage effect"—was long ago suggested by Rabinowitch.[5] The results obtained by Noyes and coworkers from their investigations of iodine atom recombination rates[6,7] and the wavelength dependence of the quantum yield for iodine photodissociation[8–10] in solution also suggest that these short-range correlations may have a measurable effect upon the kinetics of certain very fast chemical processes.

In order to obtain additional information regarding the microscopic structure and kinetics characteristic of simple liquids, one of the authors (P. L. F.) has recently completed a series of computer calculations simulating the dynamics of a two-dimensional dense fluid of Lennard-Jones disks. Two previous papers have presented the results from some preliminary analyses of the simulation data[11] and a detailed investigation of the mechanism for diffusion and relative diffusion in the model fluid.[12] The purpose of this paper is to examine the

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[1] This work was supported in part by a grant from the National Science Foundation, No. GP-7258.

[2] Koninklijke/Shell Laboratorium, Amsterdam, Holland.

[3] M. von Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

[4] R. M. Noyes in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p 128.

[5] E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937); W. C. Wood, *ibid.*, **32**, 1381 (1936).

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[7] R. M. Noyes, *ibid.*, **86**, 4529 (1964).

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[9] L. F. Meadows and R. M. Noyes, *ibid.*, **82**, 1872 (1960).

[10] R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).

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[12] P. L. Fehder, C. A. Emeis, and R. P. Futrelle, "The Microscopic Mechanism for Self-Diffusion and Relative Diffusion in Simple Liquids," manuscript in preparation.

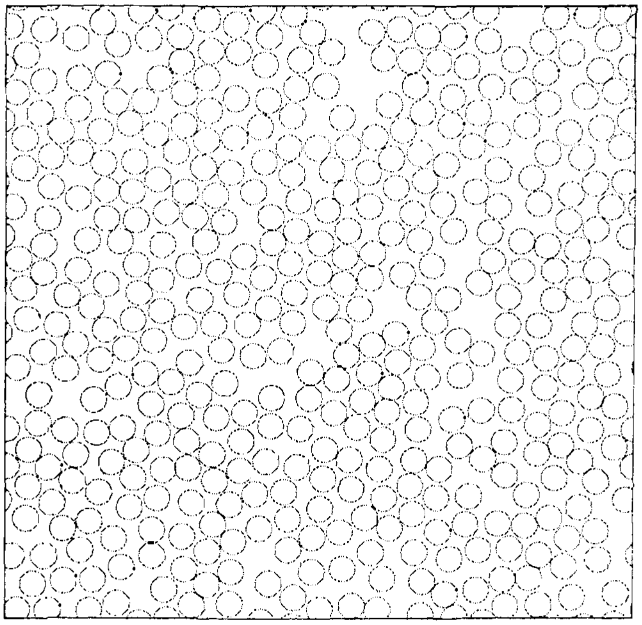

Figure 1. "Snapshot" of an instantaneous configuration of the model fluid in a liquid-like state. The particles are plotted with a diameter σ, the distance parameter in the Lennard-Jones pair potential.

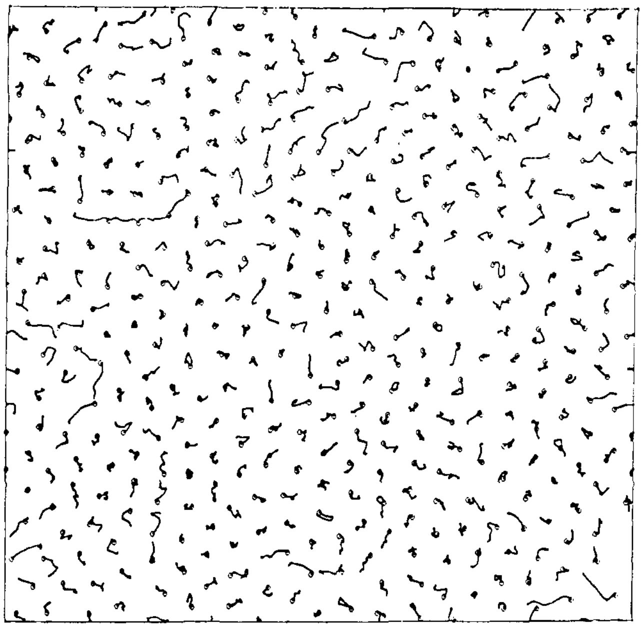

Figure 2. Trajectories of the particles in a liquid-like state of the model fluid. The small circles mark the initial positions of the particles, and the irregular lines extending therefrom the paths of the centers during the remainder of a 2×10^{-12} sec interval. The initial configuration also corresponds to that shown in Figure 1.

impact of previous findings upon the treatment of diffusion-controlled reaction kinetics in solution. Related topics, such as the solvent cage effect and the wavelength dependence of quantum yields for photodissociation in solution will also be discussed briefly.

Diffusion in Simple Liquids

Examination of graphical displays of the simulation data has led to several intuitively important observations regarding the microscopic character of simple liquids. For example, "snapshots"[13] of the instantaneous configuration of the model system (see, *e.g.*, Figure 1) provide evidence that the "excess" volume acquired by a liquid through thermal expansion is localized into relatively large, irregular "holes." Although a number of theories of the liquid state[14] have postulated the existence of holes in the microstructure of real liquids, the phenomenon observed differs from that suggested by the theoretical models in two significant ways: (i) the holes appearing in the model fluid bear no relationship to the size and shape of an individual fluid particle (that is, the holes do *not* appear as "vacancies" in an otherwise quasi-crystalline structure), and (ii) comparison of snapshots for successive times shows that a given hole may persist in the same region of the fluid for times of the order of 5×10^{-12} sec—well in excess of the characteristic kinetic relaxation time (*ca.* 2.5×10^{-13} sec) for the system. A more detailed analysis of the microscopic structure of the model fluid, and the relationship between this structure and the structure of real simple liquids, is presented elsewhere.[15]

Plots such as those shown in Figure 2 of the trajectories of the particles in the model fluid provide some insight into the microscopic mechanism for diffusion in simple liquids. As can be seen in the figure, extensive diffusive migration is—over a surprisingly long time interval—largely restricted to local groups of particles in the region of a hole. Furthermore, motion pictures created from the simulation data show that the local groups of long trajectories arise from a *concerted* migration of the particles involved, rather than from successive "jumps" or knock-on collisions. Diffusion in the model fluid therefore proceeds by a mechanism that is largely cooperative in nature, and it is reasonable to assume that similar cooperative phenomena occur in real liquids.

Although it is unlikely that cooperative phenomena of the sort observed in the model fluid would have a *macroscopically* discernible effect upon singlet[16] diffusion in real liquids, the short-range correlations associated with these phenomena become more important when the *relative* diffusion of molecules in solution is examined. It is convenient to describe relative diffusion in terms of the motion of one molecule in a coordinate system fixed to the center of the other; in two dimensions, the relative diffusion tensor $\mathbf{D}_{\mathrm{R}}$ then has the form

$$\mathbf{D}_{\mathrm{R}} = \begin{pmatrix} D_{\mathrm{rr}} & 0 \\ 0 & D_{\theta\theta} \end{pmatrix}$$

where D_{rr} and $D_{\theta\theta}$ are the coefficients for radial and tangential diffusion, respectively, and the off-diagonal elements of the tensor vanish by symmetry.

Consider a solution of two solute species, X and Y, in a solvent S. It is easily shown[12] that, if the diffusive motions of the X and Y molecules are completely

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(13) A detailed description of the graphical display techniques employed in analysis of the simulation data is provided in ref 11.

(14) See, for example, H. Eyring and R. P. Marchi, *J. Chem. Educ.*, **40**, 562 (1963), and the discussion in J. M. H. Levelt and E. G. D. Cohen in "Studies in Statistical Mechanics," Vol. 2, J. deBoer and G. E. Uhlenbeck, Ed., North-Holland Publishing Co., Amsterdam, Holland, 1964, p 178 ff.

(15) P. L. Fehder, *J. Chem. Phys.*, **52**, 791 (1970).

(16) We use the word "singlet" here to distinguish between the migration of individual molecules in solution and the *relative* diffusion of pairs of molecules.

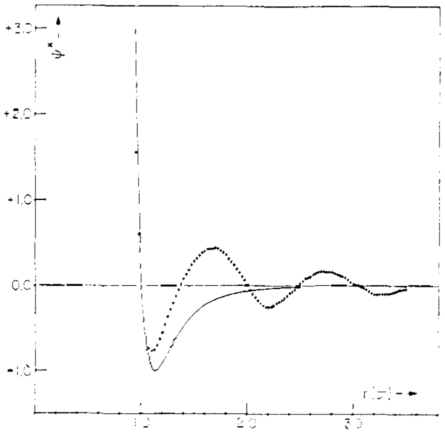

Figure 3. Comparison of the mean potential $\psi(r)$ calculated for the liquid-like state of the model fluid shown in Figures 1 and 2 and the Lennard-Jones pair potential used in the simulation calculations.

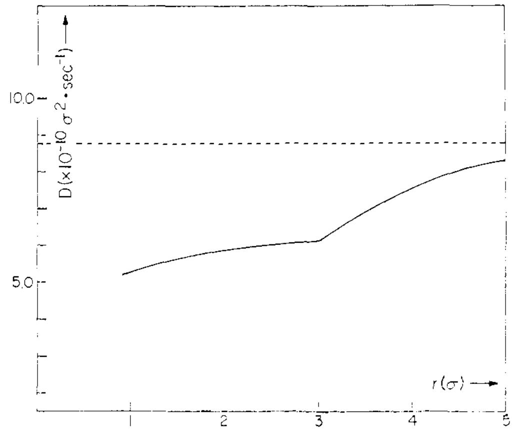

Figure 4. The empirically determined radial relative diffusion coefficient $D_{rr}(r)$ for the liquid-like state of the model fluid shown in Figures 1 and 2. The dashed line represents the usual assumption that $D_{rr} = 2D_s$.

uncorrelated, the coefficients describing the diffusion of X molecules relative to Y molecules (or *vice versa*) are just equal to the sum of the bulk diffusion coefficients for X and Y in S. In statistical terms,[17] this means that the average square of the time-dependent displacements of an X molecule relative to a Y molecule (or *vice versa*) is just the sum of the time-dependent mean square displacements of the X and Y molecules taken separately. And by analogy, if no correlations exist between the motions of molecules in a one-component fluid, the coefficients D_{rr} and $D_{\theta\theta}$ describing the relative diffusion of pairs of the molecules would both be equal to just twice the coefficient D_s for self-diffusion.

Particles separated by large distances in the model fluid diffuse independently. But analysis of the simulation data has also shown[12] that short-range "cooperative" correlations slow the relative motions of molecules approaching to within about 3-4 diameters of each other. A similar phenomenon had previously been suggested by Noyes;[7] in terms of chemical reaction kinetics in solution, this result implies that the standard Smoluchowski-type treatments may overestimate the frequency of reactant-pair encounters—and thus, overestimate the rates of so-called "diffusion-controlled" reactions. Conversely, the computer results also indicate that encounter pairs will remain in close proximity appreciably longer than predicted by an "independent" diffusion model. In the case of reactions having a non-negligible activation energy or those requiring a specific steric configuration of the reactant molecules, the depressed rate of reactant encounter may therefore be offset by an increased probability of reaction upon encounter.

To a good approximation, relative diffusion in solution may be treated in terms of the mean potential $\psi(r)$ acting between two molecules when interactions with the surrounding solvent molecules are taken into account. A convenient form for the mean potential in a one-component liquid is obtained from the familiar radial distribution function $g(r)$[18]

$$\psi(r) = k_B T \ln g(r) \qquad (1)$$

where k_B is the Boltzmann constant and T the temperature. The radial distribution function for the model fluid has been discussed in detail elsewhere.[15] In Figure 3, the mean potential obtained *via* eq 1 for a liquid-like state of the model fluid is shown in comparison with the Lennard-Jones pair potential.

$$\phi_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (2)$$

used in the simulation calculations. Unlike the simple pair potential, $\psi(r)$ exhibits a number of subsidiary maxima and minima corresponding to the first, second, . . ., etc., "shells" of neighbors surrounding a molecule in a liquid. Thus, in the mean potential model for relative diffusion, a molecule diffusing toward another molecule in solution must cross successively higher potential "barriers" before the two molecules come into direct contact.

Numerical solutions of the two-dimensional diffusion equation including $\psi(r)$ have shown[12] however that the mean potential is not in itself sufficient to account for the relative diffusion phenomena observed in the model fluid; to obtain agreement with the simulation data it was also necessary to lower the value of D_{rr} for pairs of particles separated by short distances. Although the precise physical meaning of this *empirical* variation in the relative diffusion coefficient is not entirely clear, we believe that it reflects the inability of a time-averaged function like $\psi(r)$ to account completely for the role played by transient geometric or "excluded volume" effects in the microscopic mechanism for diffusion at liquid-like densities. The two-dimensional diffusion equation including both $\psi(r)$ and a relative diffusion coefficient $D_{rr}(r)$ of the form shown in Figure 4 was found to reproduce quite accurately the relative diffusion phenomena observed in the model fluid.

Reaction Kinetics in Solution

In this section we obtain expressions describing the rates of so-called diffusion-controlled reactions in two- and three-dimensional solutions. The derivation follows closely that presented by Noyes,[4] but is extended to take into account both the mean force and the functional $D_{rr}(r)$ discussed above. The physical reasoning

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[17] See, for example, R. Zwanzig, *Annu. Rev. Phys. Chem.*, 16, 67 (1965).

[18] P. A. Egelstaff, "An Introduction to the Liquid State," Academic Press, New York, N. Y., 1967, p 16.

in support of this treatment has been discussed in detail elsewhere[7,19–21] and will not be reproduced here.

Three-Dimensional Solution. Consider again the solution of two solute species, X and Y, in solvent S. Let us assume that the X and Y molecules exert no long-range forces on each other, and that initially the molecules of each species are distributed randomly throughout S in the way they would be if the other species were not present. Furthermore, let us assume that at some zero time we can "turn on" a diffusion-controlled reaction X + Y → products in the solution. We wish then to calculate the rate of the reaction at subsequent times.

Very soon after the reaction is initiated, most of the X molecules that were near Y molecules at $t = 0$ will have reacted so that the concentration of Y molecules near a still-unreacted X will, on the average, be somewhat lower than the remaining bulk concentration of Y in the solution. This situation is then analogous to the existence of a concentration gradient in Y around the remaining X molecules. In most systems of chemical interest, a steady-state condition is quickly achieved such that the next flux Φ of Y molecules toward X molecules along this gradient is the same at all distances away from the centers of the X molecules and is just sufficient to provide for the rate at which the X molecules react. If $c(r)$ is the average concentration of Y at a distance r from the center of an X molecule, the flux of Y molecules through a sphere of radius r about an X is given by

$$\Phi = 4\pi r^2 D_{\mathrm{rr}}(r)\left[\frac{\partial c(r)}{\partial r} + \frac{c(r)}{k_{\mathrm{B}}T}\frac{\mathrm{d}U(r)}{\mathrm{d}r}\right] \qquad (3)$$

where $D_{\mathrm{rr}}(r)$ is the radial coefficient for the relative diffusion of X and Y molecules, and $U(r)$ is the potential of the mean force acting on X–Y pairs in the solution. But in steady state, this net flux must be balanced by the rate at which Y molecules are depleted from solution by reaction

$$\Phi = kc(\rho)\exp(U(\rho)/k_{\mathrm{B}}T) \qquad (4)$$

where ρ is the X–Y distance at which reaction can occur, and k is the rate constant that would be observed were an equilibrium distribution of solute molecules maintained in the system.

Combining eq 3 and 4 and solving for the steady-state concentration yields

$$c(r) = \exp(-U(r)/k_{\mathrm{B}}T)[c(\infty) - \frac{kc(\rho)}{4\pi(rD)^*}\exp(U(\rho)/k_{\mathrm{B}}T)] \qquad (5)$$

where the quantity $(rD)^*$ is given by

$$(rD)^* = \left[\int_r^{\infty}\exp(U(s)/k_{\mathrm{B}}T)\frac{\mathrm{d}s}{D_{\mathrm{rr}}(s)s^2}\right]^{-1} \qquad (6)$$

The microscopic distribution $c(r)$ is not accessible to direct experimental measurement. Instead, kinetics data are used to determine the macroscopic second-order rate constant k' based on the bulk concentration [Y] of Y

$$\Phi = k'[\mathrm{Y}] \qquad (7)$$

To a good approximation, [Y] in eq 7 may be equated with $c(\infty)$. Comparison of eq 4 and 7 then shows that

$$c(\infty) = \frac{k}{k'}c(\rho)\exp(U(\rho)/k_{\mathrm{B}}T) \qquad (8)$$

Substituting this result into eq 5 with $r = \rho$ and rearranging, we obtain the final expression

$$k' = \frac{k}{1 + (k/4\pi(\rho D)^*)} \qquad (9)$$

which differs from the expression obtained by Noyes[4] in that the quantity $(\rho D)^*$, defined in eq 6 at $r = \rho$, is calculated with reference to the mean potential $U(r)$ and an r-dependent coefficient $D_{\mathrm{rr}}(r)$.

For reactions of the type, X + X → products, the right-hand sides of eq 4 and 7 must be multiplied by a factor of 2, leading to

$$k' = \frac{k}{1 + (k/2\pi(\rho D)^*)} \qquad (10)$$

Two-Dimensional Solution. If we attempt to carry out a similar derivation for the rate of reaction in a two-dimensional solution, we quickly come upon a striking difference between the situations in two and three dimensions. For the sake of simplicity, let us first assume that D_{rr} is independent of r, and that any interaction $U(r)$ between X and Y molecules can be ignored. Then in two dimensions the steady-state condition is represented by

$$kc(\rho) = 2\pi r D_{\mathrm{rr}}\frac{\partial c(r)}{\partial r} \qquad (r > \rho) \qquad (11)$$

Equation 11 is identical with the expression obtained for three dimensions by equating the right-hand sides of eq 3 and 4, except that the factor $2\pi r$ for the circumference of a circle appears in place of $4\pi r^2$, the surface area of a sphere.

Integration of eq 11 yields the result

$$c(r) = c(\rho)[1 + (k/2\pi D_{\mathrm{rr}})\ln(r/\rho)] \qquad (12)$$

which indicates that $c(\infty)$ must be infinite if a steady-state condition is to be maintained. We conclude that diffusion in two dimensions does not provide a sufficient supply of inflowing Y molecules to sustain a steady-state concentration gradient. (The same conclusion obtains if the mean potential $U(r)$ and variations in $D_{\mathrm{rr}}(r)$ can be neglected for X–Y distances greater than some value R. Equations 11 and 12 are then valid for $r > R$, requiring that $c(\infty)$ be infinite for a steady-state condition to be achieved.) The concentration $c(\rho)$—and hence the observed rate of reaction k'—must therefore decrease monotonically with increasing time until reaction is complete.

In contrast to eq 8, the *time-dependent* macroscopic rate factor $k'(t)$ for a diffusion-controlled reaction in two dimensions is given by

$$k'(t) = \frac{c(\rho,t)}{kc(\infty)}\exp[U(\rho)/k_{\mathrm{B}}T] \qquad (13)$$

for times t sufficiently short that the bulk concentration of Y (here approximated by $c(\infty)$) does not change appreciably. Solutions to eq 13 can then be obtained

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(19) P. Debye, *Trans. Electrochem. Soc.*, 82, 265 (1942).

(20) F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, 4, 425 (1949).

(21) F. C. Collins, *ibid.*, 5, 499 (1950).

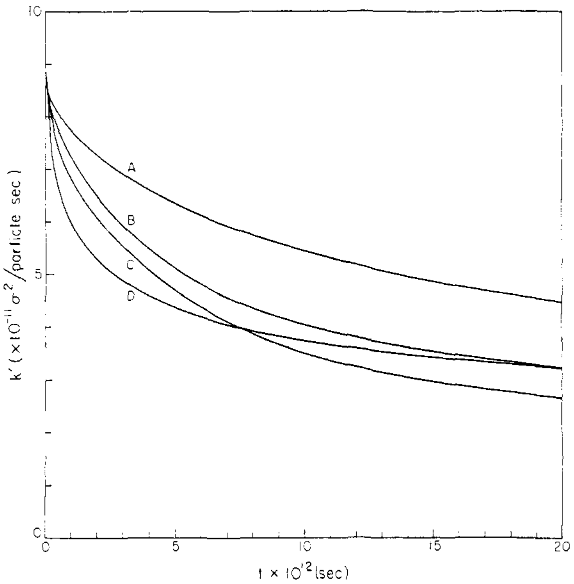

Figure 5. Plot of the time-dependent macroscopic rate constants for a diffusion-controlled reaction in two dimensions. The mathematical assumptions leading to each of the four curves are identified in the text.

by numerical integration of the system of equations

$$\frac{\partial c(r,t)}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left\{rD_{\rm rr}(r)\left[\frac{\partial c(r,t)}{\partial r} + \frac{c(r,t)}{k_{\rm B}T}\frac{{\rm d}U(r)}{{\rm d}r}\right]\right\} \quad (14a)$$

$$\frac{\partial c(\rho,t)}{\partial t} = -kc(\rho,t)\exp[U(\rho)/k_{\rm B}T] \quad (14b)$$

from the initial condition

$$c(r,0) = c(\infty)\exp[-U(r)/k_{\rm B}T] \quad (15)$$

where (14a) is the diffusion equation in two dimensions and (14b) accounts for the depletion of Y molecules due to reaction.

Results

Rate factors k' for a diffusion-controlled reaction $X + Y \rightarrow$ products in two- and three-dimensional solutions were computed for a variety of combinations of $D_{\rm rr}(r)$ and $U(r)$. It was assumed that the species X and Y distinguish themselves from the solvent only in their ability to react with each other; otherwise, the potential $U(r)$ and the relative diffusion coefficient $D_{\rm rr}$ for an X–Y pair were assumed to be the same as for a pair of solvent molecules. The "equilibrium" rate constants k were calculated from two- and three-dimensional kinetic gas theory with the assumption that every collision would result in reaction. The distance ρ at which reaction can occur was taken equal to the σ parameter in the Lennard-Jones pair potential.

Two-Dimensional Solution. The rate calculations for two dimensions were based on the liquid-like state of the model fluid shown in Figures 1 and 2 and examined in detail in ref 12. The value of the self-diffusion coefficient for this state is $D_{\rm s} = 4.39 \times 10^{10}\sigma^2$ sec^{-1}; the potential of the mean force $\psi(r)$ is shown in Figure 3, and the empirically determined relative diffusion coefficient is that shown in Figure 4.

The time-dependent behavior of $k'(t)$ for four different $D_{\rm rr}(r)$–$U(r)$ combinations is shown in Figure 5. In order to determine the effect of the interaction $U(r)$ on the rate of reaction, $k'(t)$ was calculated with a fixed value of $D_{\rm rr} = 8.78 \times 10^{10}\sigma^2$ sec $= 2D_{\rm s}$ for $U(r > \rho) = 0$ (curve D), $U(r) = \psi(r)$ (curve B), and for $U(r)$ equal to the Lennard-Jones pair potential $\varphi_{\rm LJ}(r)$ (curve A). Curve C was obtained with $U(r) = \psi(r)$ and $D_{\rm rr}(r)$ as shown in Figure 4. Curve C therefore represents the most accurate evaluation of $k'(t)$ for a diffusion-controlled reaction in the model fluid.

During the first stage of the reaction, the rate is primarily determined by the equilibrium ($t < 0$) concentration of closely associated X–Y pairs provided by $U(r)$ according to eq 15. But after a brief induction time these initial pairs are depleted from solution by reaction, and the rate thereafter is determined by the rate at which new encounter pairs are formed through diffusion. The Lennard-Jones potential, which provides both the highest initial concentration of X–Y pairs and the least resistance to relative diffusion, yields the highest reaction rate (curve A) over the entire 2×10^{11} sec interval spanned by Figure 5. Comparison of curves A and B shows the effect upon the reaction rate of the barriers to relative diffusion provided by the mean potential $\psi(r)$, while curve C indicates the additional lowering of the reaction rate that is obtained when the "adjusted" coefficient $D_{\rm rr}(r)$ is included in the calculations.

Three-Dimensional Solution. Liquid argon at a temperature 108.18°K and density 1.261 g cm^{-3} was used as a model for the reaction system in the three-dimensional rate calculations. The radial distribution function $g(r)$ for this state has been measured by Smelser,[22] and a tabulation of the function was kindly provided by that author. The Lennard-Jones potential parameters for argon are $\sigma = 3.405$ Å, $\epsilon/k_{\rm B} = 119.80$ °K,[23] and the self-diffusion coefficient for argon in this state is $D_{\rm s} = 4.37 \times 10^{-5}$ cm^2 sec^{-1}.[24] From these parameters a value $k = 3.70 \times 10^{11}$ l. mol^{-1} sec^{-1} is obtained for the equilibrium constant.

The predicted values for k' obtained from eq 6 and 9 for several combinations of $U(r)$ and $D_{\rm rr}(r)$ are listed in Table I. Standard theoretical treatments of chemical reaction kinetics in solution generally neglect any mean pair potentials or excluded volume effects that might interfere with the relative diffusion of the reactant molecules. To determine the effect of including a reactant-pair potential in the calculations, k' was computed for $U(r > \rho) = 0$, $U(r) = \psi(r)$, and $U(r)$ equal to the Lennard-Jones potential with $D_{\rm rr}$ constant and equal to $2D_{\rm s}$ for all X–Y distances. Comparison of the values obtained for $U(r) = 0$ and $U(r) = \psi(r)$ shows that the predicted rate of reaction in three dimensions is not changed appreciably when a quasi-realistic interaction like $\psi(r)$ is incorporated into the theory.

Although the magnitude of short-range cooperative correlations in the relative diffusion of molecules in real liquids is not known and is not presently accessible to direct experimental measurement, some *estimate* of the effect these correlations would have upon the kinetics of diffusion-controlled reactions is obtained by calculating k' under the assumption that $D_{\rm rr}(r)$ for

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[22] S. Smelser, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1969. To be made available through University Microfilms.

[23] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York, N. Y., 1954, p 165.

[24] J. Naghizadeh and S. A. Rice, *J. Chem. Phys.*, 36, 2710 (1962).

Table I. Calculated Steady-State Rate Constants for a Diffusion-Controlled Reaction in Liquid Argon

$U(r)$	$D_{rr}(r)$	$(\rho D)^*$, cm^3 sec^{-1}	k', l. mol^{-1} sec^{-1}
0	$2D_s$	2.12×10^{-12}	1.00×10^{10}
$\psi(r)$	$2D_s$	2.23×10^{-12}	1.03×10^{10}
Lennard-Jones	$2D_s$	2.67×10^{-12}	1.14×10^{10}
0	As shown in Figure 4	1.50×10^{-12}	0.79×10^{10}
$\psi(r)$		1.60×10^{-12}	0.83×10^{10}
Lennard-Jones		1.96×10^{-12}	0.95×10^{10}

the three-dimensional solution varies as the ratio $D_{rr}(r)/2D_s$ observed in the two-dimensional model fluid. The final three entries in Table I show the effect of $U(r)$ when the rate constant is calculated with a coefficient $D_{rr}(r)$ that decreases for small reactant-pair separations as shown in Figure 4. For each of the three assumed forms for $U(r)$, the predicted value for k' is lowered about 20% when the r-dependent coefficient is included in the calculations.

The small change in k' that is obtained when $\psi(r)$ is included in the calculations probably reflects the partial cancellation of two opposing effects. As in two dimensions, the barriers to relative diffusion presented by an oscillatory potential like $\psi(r)$ would tend to *decrease* the rate of reaction. Yet any potential having an attractive component extending beyond $r = \rho$ would tend to increase the minimum distance within which a pair of molecules would have to approach each other before reaction becomes probable, and hence would tend to *increase* the reaction rate. This latter effect is illustrated by the relatively large increase in k' that is obtained when $U(r)$ is set equal to the Lennard-Jones pair potential and either form of $D_{rr}(r)$ is assumed. A similar effect is also observed in two dimensions, as may be seen by comparing curves A and D in Figure 5.

The substantial decrease in the predicted value for k' that is obtained when an r-dependent relative diffusion coefficient is incorporated into the calculations may—within the framework of the Smoluchowski model for diffusion-controlled reactions in solution—be attributed to the fact that a functional form for $D_{rr}(r)$ like that shown in Figure 4 tends to slow the relative diffusion of a pair of reactant molecules just in the region where the gradient in $c(r)$ is greatest. A more thorough analysis of this phenomenon would require an investigation of the steady-state concentration distributions that are established when various combinations of $U(r)$ and $D_{rr}(r)$ are assumed.

Discussion

In light of the results presented here and in two previous papers,[11,12] we may draw several conclusions regarding the *mechanical* influence of the solvent upon the microscopic kinetics of simple chemical reactions in solution. Data obtained from the computer simulation of a model dense fluid of Lennard-Jones disks has shown that diffusion in simple liquids may proceed by a mechanism that is, at the molecular level, largely cooperative in nature; and further, that this cooperative mechanism tends to retard the relative diffusion of molecules separated by short distances in the liquid.

For solutions in which the solute and solvent molecules are physically similar, the average force acting between a pair of solute molecules may be approximated by the mean potential $\psi(r)$ obtained from the experimentally accessible[25] radial distribution function $g(r)$ for the solvent. Our calculations have shown however that this time-averaged mean potential does not provide a complete description of the transient "excluded volume" effects that apparently play an important role in relative diffusion phenomena at liquid-like densities. A more accurate description of relative diffusion in the two-dimensional model fluid was obtained from a theoretical treatment that included both $\psi(r)$ and r-dependent relative diffusion coefficients. Unfortunately it is difficult to estimate, on the basis of the two-dimensional simulation data alone, the relative importance of short-range cooperative correlations in the mechanism for diffusion in real, three-dimensional liquids. The presence of an additional degree of freedom would be expected to decrease the dynamic importance of excluded volume effects; yet the relative diffusion of two molecules in a three-dimensional liquid must involve interactions with a much larger number of neighboring solvent molecules. Although direct experimental observation of relative diffusion phenomena in real liquids is not at present possible, analyses similar to those described in ref 12 of existing simulation data for three-dimensional model fluid[26,27] should yield some insight into the problem.

The results presented in this paper indicate that the decrease in the coefficient describing the relative diffusion of reactant-pairs separated by short distances is an important factor in determining the steady-state rate for a diffusion-controlled reaction in real systems. The mean potential $\psi(r)$ can nonetheless serve as a convenient intuitive device for interpreting a number of chemically important processes occurring in solution. In our investigation of diffusion in the simulated fluid,[12] we observed that pairs of particles diffusing away from each other tended to become "trapped" momentarily in first, second, and third nearest-neighbor positions. This phenomenon is reminiscent of the so-called "solvent cage effect," and can to a first approximation be ascribed to the successive potential barriers to relative diffusion presented by $\psi(r)$.

Photodissociation of a molecular solute is another process that "samples" the microscopic structure and dynamics of the solvent in local regions of a solution. Noyes and Meadows[9] have investigated the wavelength dependence of the quantum yield for photodissociation of molecular iodine in a number of nonreactive solvents and determined[10] that *the experimental results are not reproduced by a theoretical model that neglects the microscopic structure of the solvent surrounding the reaction site.* For longer wavelengths—such that the excess energy over that required to break the iodine–iodine bond is small—the simple "solvent continuum" theory is found to predict quantum yields *larger* than those observed experimentally; yet for progressively shorter wavelengths the observed quantum yield is found to increase more rapidly than predicted by the theory.

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On the basis of the model for relative diffusion phenomena presented in this paper, the experimental quantum yield data can be interpreted in terms of transient processes dependent upon the iodine–solvent interaction described by $\psi(r)$ and longer lived processes dependent upon $D_{rr}(r)$. Immediately after dissociation, the separating iodine atoms encounter the barrier in $\psi(r)$ between first and second nearest-neighbor positions. If the excess energy provided by the exciting photon is small, the atoms are reflected from the barrier and recombine quickly; but if the excess energy is sufficient to permit the separating atoms to reach second nearest-neighbor positions, the barrier will tend to keep them apart and thus prevent recombination. Furthermore, if $D_{rr}(r)$ increases with increasing r, pairs of atoms that initially achieve a large separation will diffuse away from each other more quickly, and thus be even less likely to recombine. In reality of course, the successive maxima in $\psi(r)$ and the r-dependence of $D_{rr}(r)$ are the result of interactions between the solute iodine atoms and surrounding solvent molecules, and are truly descriptive only of an equilibrium situation. Monchick[28] has however presented a theoretical treatment of photodissociation processes that includes an "effective" potential much like $\psi(r)$, although no theory incorporating both $\psi(r)$ and an r-dependent relative diffusion coefficient has previously been treated.

Acknowledgments. We wish to thank Professor G. Wilse Robinson for his helpful discussions and his critical reading of this paper. One of the authors (C. A. E.) gratefully acknowledges the support of The Netherlands Organization for the Advancement of Pure Research (ZWO).

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Investigation of Singlet → Triplet and Singlet → Singlet Transitions by Phosphorescence Excitation Spectroscopy. VIII. Santonins

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Received September 15, 1969

Abstract: The singlet → singlet and singlet → triplet transitions in α-santonin (I), 6-episantonin (II), and 2-bromosantonin (III) have been investigated at both 77 and 4.2°K. The results may be summarized as follows. (i) Polarization measurements demonstrate that vibronic coupling between the $S(n,\pi)$ and $S(\pi,\pi)$ states is the principal source of intensity for the $S_0 \rightarrow S(n,\pi)$ transition. The magnitude of the electronically allowed contribution to the intensity appears to depend upon the molecular structure. (ii) The lowest excited triplet state in each case is identified as a $^3(\pi,\pi)$ state. (iii) The $^3(n,\pi)$ state has been observed in each compound just above (1200–1600 cm^{-1}) the $^3(\pi,\pi)$ state. The intensity in the $S_0 \rightarrow T(n,\pi)$ transition of α-santonin ($\epsilon_{max} \simeq 0.3$) is attributed to strong spin–orbit coupling with the $^1(\pi,\pi)$ state. (iv) Diffuseness observed in the $S_0 \rightarrow T(n,\pi)$ absorption spectra at 4.2°K is attributed to vibronic interaction between the $^3(n,\pi)$ state and nearly degenerate vibronic levels of the lower lying $^3(\pi,\pi)$ state. These spectroscopic observations appear to have an important bearing on the interpretation of the α-santonin photochemistry and the possible role of the $^3(n,\pi)$ and $^3(\pi,\pi)$ states in the excited state transformations.

Since they were first identified in 1944,[2] interest in triplet state molecules has grown, and this growth has been particularly rapid during the last few years. Of the many types of molecules which have been studied considerable attention has been given to organic ketones and aldehydes.[3-10] Surprisingly enough most of these studies have been concerned with aromatic carbonyl compounds and there have been relatively few studies of "simple" carbonyl-containing molecules such as enones and dienones.[8-10] Because of this, and because of the current interest in their photochemical properties, we have started a comprehensive investigation of the spectroscopic properties of a wide variety of enones and dienones. Some of our earlier studies of enones have already been published,[11,12] and more detailed results will be forthcoming.[13] In the present paper we discuss results obtained with the following three cross-conjugated dienones: α-santonin (I), 6-epi-

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