pentane rings. The values of the angles in dibenzoequinene are in agreement with those reported for C_8F_{12}.

The equations of the important least-squares planes and the angles between them are given in Table V. In dibenzoequinene, the dihedral angle between planes which contain atoms C(2), C(12), C(9′) and C(2), C(11′), C(9′) is 124.5°. This compares with the angle of 120° which was obtained in C_8F_{12}. The equivalent angle in other compounds which contain cyclobutane rings ranges from 150 to 162°. The largest deviation of an atom from the plane through atoms C(1), C(2), C(9′), C(10′) in IV is 0.003 Å, with atoms C(12) and C(11′) located approximately 1.0 Å above and below this plane, respectively. Atoms C(7), C(24), C(23), C(16) and C(10), C(11), C(12), C(13) in II are not coplanar, 0.2 Å being the largest deviation of an atom from the least-squares planes. The phenyl rings are essentially planar, 0.02 Å being the largest deviation in II, and 0.003 Å the largest deviation in IV.

Figures 10 and 11 illustrate the packing in the unit cells. Excluding hydrogens, there are no intermolecular contacts smaller than 3.75 Å in II and none less than 3.66 Å in IV. Such relatively large intermolecular separations suggest that the major distortions of the molecules from the mirror planes are probably the result of intramolecular effects or random errors, even though intermolecular effects may still be important at these separations.

Acknowledgments. The author is indebted to Dr. Jerome Karle and Dr. Isabella Karle for their assistance. Mr. Stephen Brenner aided in performing the computations.

Solvent Effects in Electroneutral Reactions. I. Combination and Disproportionation of Ethyl Radicals in Solution

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Abstract: The rate ratio k_d/k_c of the disproportionation–combination reaction couple of ethyl radicals was measured at 65° in ten different solvents. The logarithms of these ratios are linear functions of the square root of the cohesive energy density of the solvents. The reaction couple was investigated in the gas phase from -65 to $+80°$ in vessels of variable volume, and it was found that a considerable extent of the reaction proceeds by a heterogeneous mechanism. On the basis of these observations the temperature dependence of k_d/k_c in liquid and in solid reaction media is interpreted to be a consequence of a secondary thermal effect whose origin is the internal volume change of the medium. The rates of certain other polar reactions are discussed in terms of internal volume considerations.

The influence of solvents upon reaction rates and equilibria has been discussed extensively in the literature in the past few decades and, although the distinction between ionic, polar, and nonpolar mechanisms had been recognized at a rather early stage in the development of reaction rate theories, nearly all the emphasis in this connection has been placed upon ionic and highly polar reactions. Although the necessary groundwork has been laid for the quantitative treatment of the influence of solvents upon the rates of electroneutral[1] reactions and of certain other reactions which manifest similar kinetic behavior, relatively few examples of such systems have been studied in a wide range of solvents to permit meaningful generalizations.

In the discussion of solvent effects upon reaction rates, regardless of which model of a liquid one employs, at least two general factors are always necessary in the theoretical development, namely the factor giving rise to the internal volume effects and the factor giving rise to the solvation effects.[2–5] Of these two factors the first accounts for the restrictions imposed upon the spatial requirements of the reacting species by the self-cohesion of the solvent, and also for the restrictions imposed upon the external degrees of freedom of these species by the solvent due to crowding. The second factor contains all other effects, most of which, in the absence of certain specific interactions, are consequences of the dielectric properties of the solvent. However, since the multitude of molecular interaction mechanisms which are responsible for the cohesive forces in the liquid state are fundamentally electrostatic in nature and inasmuch as polarity and polarization phenomena pervade all molecular interactions, no line of demarcation separating electroneutral from polar changes can be defined in an unambiguous manner. Obviously these two factors are not mutually exclusive, but they may be treated as limiting cases of the general relations pertaining to

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(1) An electroneutral reaction is one in which all of the participating species are neither ionic nor highly polar; when studied in solution, the reacting system conforms to the principles that characterize regular solution; *cf.* J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(2) S. Glasstone, K. J. Laider, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(3) R. A. Ogg, Jr., and O. K. Rice, *J. Chem. Phys.*, **5**, 140 (1937).

(4) (a) W. F. K. Wynne-Jones and H. Eyring, *ibid.*, **3**, 492 (1935); (b) C. E. Waring and P. Becher, *ibid.*, **15**, 488 (1947).

(5) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).

problems in solubility and of solvent effects. Even though in principle solute–solvent interaction mechanisms may be enumerated and interpreted physically,[6] the principal fundamental operational difficulties in these matters lie in the problem of discerning the particular mechanisms which influence the properties of the reaction, and also of being able to measure the relative magnitudes of the contributions arising from each mechanism. These difficulties are magnified when one is dealing with mixed solvents. Nevertheless, some chemical reactions which proceed by homopolar mechanisms exhibit properties which to a first approximation can be described by the concepts arising in the consideration of internal volume effects. This conclusion was first deduced empirically by Soper and co-workers[7,8] and was later discussed from a theoretical standpoint by Glasstone[9] and also by Ogg and Rice,[3] who coined the term "internal volume factor." However, adequate experimental data have not become available to permit a test of the quantitative aspects of these ideas. The number of chemical reactions falling in this category is expected to be quite large; in fact, certain highly polar and even certain ionic reactions are also expected to fall in this category because, even though solvation effects may be the dominant factors that determine the equilibrium properties of a solution, internal volume effects will be the decisive factors if all the species involved in an activation-controlled change are stabilized to the same extent by approximately similar solute–solvent interaction mechanisms. Thus any rate process in which solvation effects are constant throughout the course of the process is expected to conform to a rate theory which is based upon the model of regular solutions.[2]

In previous communications[10] we showed that the disproportionation–combination rate ratio k_d/k_c of ethyl radicals and of the methyl–ethyl couple in solution was affected by the solvent in a manner which was in qualitative agreement with the foregoing considerations. In this paper we report further work on these reactions both in the gas phase and in solution, with major emphasis on solvent effects, and show that there is a quantitative correlation between the ratio k_d/k_c and the internal volume properties of the solvents in which the reaction was investigated.

Experimental Section

The experimental method and the analytical techniques employed in these studies were described fully in previous papers[10,11] to which the reader is referred for details.

Azoethane, acquired from Merck Co., Montreal, Canada, was purified by distillation and photolyzed in the gas phase and in solution. The gaseous photolysis was investigated at +80, +40, 0, and −65° in Pyrex glass vessels each equipped with a break-seal and a constricted ground-glass arm which permitted the vessel to be sealed off from the vacuum system. Photolysis in solution (10^{-3} *M*, 10-cc ampoules) was carried out in ten different solvents at 65° (Table I). Styrene was used as a radical scavenger when this was necessary.

The ampoules used for all the work in the liquid phase were of Pyrex glass and at one end they were drawn to a fine breakable tip. The upper part of these ampoules which was not filled by the liquid was screened with aluminum foil to prevent photolysis of the azo compound in the gas phase.

Table I. Photolysis of Azoethane in Different Solvents at 65°

	Solvent	No. of expts	Scavenger	C_2H_4/C_4H_{10}
1.	Ethylene glycol	5	None	0.241 ± 0.003
2.	Acetonitrile	6	Styrene	0.208 ± 0.006
2.	Acetonitrile	6	None	0.200 ± 0.006
3.	Aniline	5	Styrene	0.195 ± 0.001
4.	1-Propanol	5	Styrene	0.181 ± 0.003
5.	2-Propanol[a]	4	Styrene	0.178 ± 0.001
6.	2-Butanol	5	None	0.168 ± 0.001
7.	Toluene	5	None	0.167 ± 0.003
8.	*m*-Xylene	5	None	0.165 ± 0.003
9.	Ethylbenzene	5	None	0.156 ± 0.001
10.	Limonene	5	None	0.158 ± 0.005
11.	Isooctane	5	None	0.144 ± 0.003
11.	Isooctane[a]	3	Styrene	0.145 ± 0.007

[a] Data from ref 10.

All solvents employed were either spectroscopically pure or were purified by distillation and/or by liquid chromatography. Photolysis was carried out by a high-pressure mercury lamp (General Electric AH-6). Product analysis was performed with a gas chromatograph attached permanently to the vacuum system. The packing in the chromatographic columns used for analysis was either silica gel, firebrick, or alumina. The method of preparing the samples and that of collecting the products including the method of standardization of the analytical technique has been discussed elsewhere.[10,11]

Results and Discussion

Photolysis of azoethane yields almost simultaneously[10] two ethyl radicals and a nitrogen molecule. When this decomposition is carried out in solution, the two geminate radicals find themselves constrained for a brief period of time to remain in the same solvent pocket, during which time there will be a finite probability that before they diffuse apart they will react with each other. This situation is predicted by any model of a liquid, and intuitively we expect that the relative probabilities of the reaction and of the diffusive process will be governed to a large measure by the transport properties of the solution, by solvation effects if the occurrence of these influences the reaction, and by the properties of the solvent which give rise to what we described above as internal volume effects. In the investigation of the effect of the solvent upon the rate ratio k_d/k_c of the disproportionation–combination reaction couple, the occurrence of the diffusive process is of course inconsequential. The ratio k_d/k_c is given by the product ratio C_2H_4/C_4H_{10} which in any given solvent and at a constant temperature is a constant independent of the fraction of radicals escaping the primary cage.

The values of k_d/k_c obtained in this work in ten different solvents are summarized in Table I where it is seen that there is an increase of about 66% from the lowest value, in isooctane, to the highest, in ethylene glycol. The variation of the rate ratio with solvent changes is certainly not as dramatic as that observed in certain ionic reactions where solvation effects are unmistakably the dominant factors in the pertinent rate processes. But it is what one might expect from an electroneutral reaction, although we cannot justifiably rule out completely solvation effects. The latter, however, if they influence the reaction at all, must be of negligible im-

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(6) G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 1486, 2314 (1934).

(7) M. Richardson and F. G. Soper, *J. Chem. Soc.*, 1873 (1929).

(8) F. G. Soper and E. Williams, *ibid.*, 2297 (1931).

(9) S. Glasstone, *ibid.*, 723 (1936).

(10) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551, 3344 (1963).

(11) A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

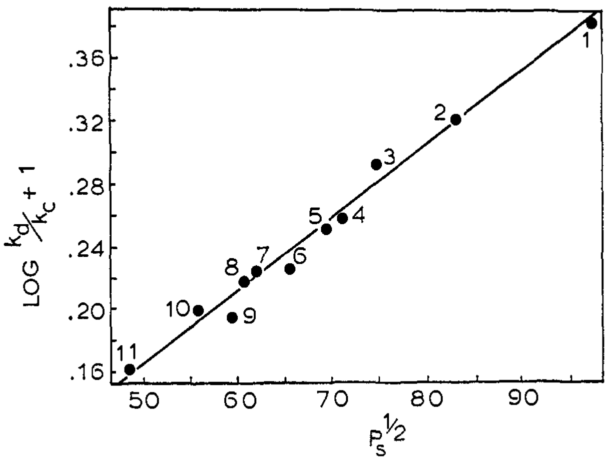

Figure 1. Combination and disproportionation of ethyl radicals in solution. Log (k_d/k_c) as a function of the square root of the internal pressure of the solvent.

portance; indeed, there is no obvious quantitative relation between our data and the dielectric properties of the solvents.

Reaction rates in solution involving nonpolar and also neutral polar molecules have been discussed by Eyring and co-workers[2,12] on the basis of the transition-state theory. For such reactions the recognizable solute–solvent interactions which produce the consequent solvation effects are those involving the dielectric properties of the solvent–solute system and the short-range van der Waals forces, both of which may be described in terms of dielectric constants ϵ, dipole moments μ, quadrupoles q, and polarizabilities α. The general relation for the specific rate k' of the reaction may be written as

$$kT \ln k' = f(\epsilon, \mu_i, q_i, \alpha_i, r_i) + \Sigma\phi_i + \text{constant} \quad (1)$$

where k is the Boltzmann constant and r_i is the molecular radius. The first term on the right-hand side is the contribution due to solvation effects. The second term is a nonelectrostatic contribution which we interpret to the internal volume factor whose magnitude, at constant temperature and constant external pressure, will depend on the solvent and whose origin is the cohesive energy density of the solvent. (In many cases additional specific solute–solvent interactions, such as hydrogen bonding, must also be considered.) The parameters ϕ_i have the units of energy which in this case is the interchange energy between solute and solvent molecules and which in thermodynamic language becomes the partial molar heat of solution given by the expression $V_i(P_i^{1/2} - P_s^{1/2})^2$, where V_i is the molar volume of the solute i, and P_i and P_s are respectively the internal pressures (or cohesive energy densities) of the solute and of the solvent.[13] The summation in eq 1 may be interpreted as the term representing the change in energy which is generated by virtue of the constraints imposed by the cohesion of the solvent upon the volume relationships of the reactants and of the transition state. For a reaction between nonpolar molecules, the importance of the solvation factor will depend mainly on the magnitude of the short-range van der Waals forces or, more precisely, on the difference between the solvation energy of the transition state and of the reactants, and even for small molecules this factor is not zero; however, its relative importance is small, and here we shall assume that it is negligible. Thus eq 1 reduces to

$$RT \ln k' = \Sigma V_i(P_i^{1/2} - P_s^{1/2})^2 + \text{constant} \quad (2)$$

For the cage reaction between two geminate ethyl radicals as depicted by eq A, the explicit functional

$$(2C_2H_5) \begin{array}{l} \xrightarrow{k_d} C_2H_4 + C_2H_6 \\ \xrightarrow{k_c} C_4H_{10} \end{array} \quad (A)$$

relation for the rate ratio k_d/k_c takes the form

$$RT \ln (k_s/k_g) = (V_d - V_c)P_s - 2(V_dP_d^{1/2} - V_cP_c^{1/2})P_s^{1/2} + (V_dP_d - V_cP_c) \quad (3)$$

where the pressures and volumes marked with subscripts c and d represent quantities pertaining to the combination and to the disproportionation transition states, and k_s and k_g are the rate ratios k_d/k_c in solution and in the gas phase, respectively. Equation 3 is quadratic of the form $y = ax^2 + bx + c$, with $x = P_s^{1/2}$, which may be transformed into the linear eq 4 by making the not unreasonable assumption that $V_d = V_c = V$.

$$RT \ln (k_s/k_g) = 2V(P_c^{1/2} - P_d^{1/2})P_s^{1/2} - V(P_c - P_d) \quad (4)$$

The application of eq 4 to our data is shown in Figure 1. The values of internal pressures for the solvents employed in this study were taken from the tabulations of Hildebrand and Scott[13] or were calculated by using Hildebrand's methods which yield values of quite good accuracy. The equation of the line in Figure 1 is given by

$$\log (k_d/k_c) = -1.08 + (4.76 \times 10^{-3})P_s^{1/2} \quad (5)$$

and we see that within the validity of the approximations made the internal pressure of the combination transition state is larger than that of the disproportionation transition state. Assuming that the gas-phase value of k_d/k_c is 0.13, the quantities $V(P_c - P_d)$ and $V(P_c^{1/2} - P_d^{1/2})$ respectively are calculated to be 12.1 and 0.152. Now the value of the molar volume V, under the experimental conditions (65°), is very likely to lie between that of butane (~100 cc) and twice that of ethane (~140 cc), but there are good reasons to believe that it lies close to the latter values.[14,15] Thus we estimate that the difference ($P_c - P_d$) is less than 100 atm and that the difference ($P_c^{1/2} - P_d^{1/2}$) is approximately equal to 1. This means that the two transition states are essentially alike and that, if they differ at all in their potential energies, they differ only by a few kT. This conclusion finds support in the fact that the rate ratio k_d/k_c in the gas phase is independent of the frequency of deactivating collisions and independent of the efficiency of inert molecules acting as energy-transfer agents.[10]

The nature of the transition states involved in this combination–disproportionation reaction couple has

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(12) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

(13) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(14) R. A. Marcus, *J. Chem. Phys.*, **20**, 364 (1952).

(15) O. K. Rice, *J. Phys. Chem.*, **65**, 1588 (1961).

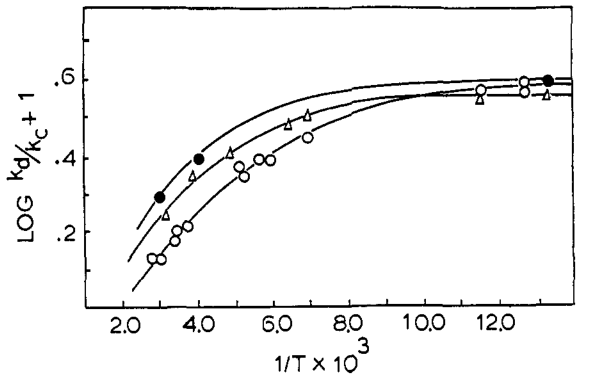
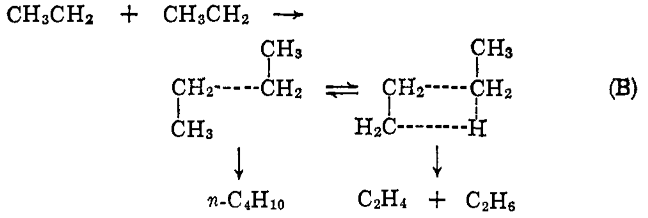


Figure 2. Photolysis of azoethane in isooctane, in 2-propanol–1-propanol, and in ethylene glycol log (k_d/k_c) *vs.* 1/*T*: ○, isooctane; △, 2-propanol; ●, glycol.

been discussed recently, for the case of a gaseous system, by Bradley[16] and also by Kerr and Trotman-Dickenson,[17] who suggested that the two competing processes pass through a common set of intermediates of the type implied by the equilibrium of the two partially bonded subspecies in eq B. Although our present data and



$$CH_3CH_2 + CH_3CH_2 \rightarrow \begin{matrix} \overset{CH_3}{\overset{|}{CH_2}}\text{-----}CH_2 \\ | \\ CH_3 \end{matrix} \rightleftharpoons \begin{matrix} \overset{CH_3}{\overset{|}{CH_2}}\text{-----}CH_2 \\ | \qquad\quad | \\ H_2C\text{--------}H \end{matrix} \quad (B)$$

$$\downarrow \; n\text{-}C_4H_{10} \qquad \downarrow \; C_2H_4 + C_2H_6$$

our interpretation have a direct bearing on the controversy regarding the problem of a head-to-tail *vs.* a four-center disproportionation transition state,[18] we do not mean to imply that we have solved the problem, if one ever existed, but we do take the view that the mechanism implied by eq B is correct. In fact, the solution to this problem was made evident by Marcus[14] and by Rice[15] in terms of the uncertainty principle, as soon as the problem was invented. Our data suggest that the two transition states are very similar, very much like the initial radical pair, and hence they are rather loose. Our data also suggest that the temperature dependence of the rate ratio k_d/k_c in the gas phase which we observed in our earlier study[10] might have been fortuitous. This latter suggestion was sufficient reason for us to reinvestigate the gas-phase reaction. Table II is a summary of our more recent data which leave no doubt that in the gas phase there is a heterogeneous component in the mechanism of formation of the products of the disproportionation–combination reaction system. Apparently the importance of the heterogeneous component is greater at the lower temperatures. There is no question that the rate ratio k_d/k_c depends on temperature, and although this dependence cannot be determined from our data it must be very small indeed. That this is so is evident from the results of practically all workers who have investigated this system and who concluded that the temperature coefficient is very nearly zero. A review of the pertinent work in this connection has been given by Trotman-Dickenson.[19]

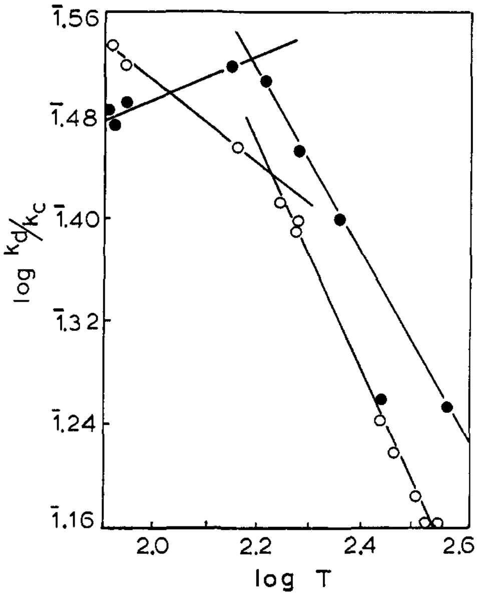


Figure 3. Photolysis of azoethane in toluene and in isooctane. Log (k_d/k_c) *vs.* log *T*: ○, isooctane; ●, toluene.

Table II. Combination and Disproportionation of Ethyl Radicals in the Gas Phase, the Effect of the Surface-to-Volume Ratio

V, cc	Temp, °C	No. of expts	k_d/k_c
1160	−65	3	0.148 ± 0.005
725	−65	4	0.158 ± 0.005
250	−65	5	0.185 ± 0.005
100[a]	−65	3	0.255 ± 0.022
1160	0	3	0.119 ± 0.005
725	0	4	0.131 ± 0.005
250	0	3	0.155 ± 0.005
1160	+40	2	0.127 ± 0.005
250	+40	2	0.155 ± 0.005
1165	+80	2	0.123 ± 0.005
725	+80	3	0.121 ± 0.005
250	+80	4	0.134 ± 0.005

[a] Packed with small pieces of broken glass tubing.

In light of the above considerations and of our conclusions in regard to the effect of the solvent upon the ratio k_d/k_c, we shall now elaborate upon a question which we raised in our earlier communication[10] concerning the effect of solid reaction media upon the ratio k_d/k_c, and in particular concerning the peculiar behavior of this ratio when studied as a function of temperature in a given solvent. The graphical representation of our earlier data in terms of an Arrhenius plot is reproduced in Figure 2 which clearly shows that the ratio k_d/k_c increases with decreasing temperature and that the rate of change of k_d/k_c is greater at the higher temperatures. If each of the curves in Figure 2 is treated as two intersecting straight lines separating the experimental points into two sets, the point of intersection of the two lines occurs at about the melting point of the solvent. This is shown more clearly in Figure 3.

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(16) J. N. Bradley, *J. Chem. Phys.*, **35,** 748 (1961).

(17) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Chemical Kinetics," Vol. 1, Pergamon Press, New York, N. Y., 1961.

(18) J. R. McNesby, C. M. Drew, and A. S. Gordon, *J. Phys. Chem.*, **59,** 988 (1955).

(19) A. F. Trotman-Dickenson, "Free Radicals," Methuen and Co., London, 1959.

Now the most obvious explanation of this curvature may be that in the vicinity of the solidification temperature of the medium there is a change in the reaction mechanism. But, assuming the validity of our conclusions in regard to the nature and the source of the influence which the medium bears upon this strictly nonpolar reaction, it is difficult to see how solidification of the medium can effectively bring about a change in mechanism. However, there are certain significant differences between solids and liquids which themselves suggest the clue to the answer. A solid differs from a liquid by the fact that in the former the rate of mass transport is much slower than that in the latter; furthermore, the compressibility or, what is more relevant to this problem, the coefficient of thermal expansion, $\alpha = (1/V_0)(\delta V/\delta T)$, of solids is smaller than that of liquids, and in fact the ratio $\alpha_{\text{liq}}/\alpha_{\text{solid}}$ is about 10. Both of these phenomena may be accounted for in terms of free volume or hole theories of liquids, and the connection of these phenomena to the quantity $(\delta E/\delta V)$ of the solvents with which we already correlated our data needs no further comment other than to stress the fact that, within certain limits, as the molar volume of a given liquid or solid diminishes the internal pressure $P_i = \delta E/\delta V$ increases and consequently the ratio k_d/k_c also increases, as we have already demonstrated. In view of this we may anticipate that the ratio $\alpha_{\text{liq}}/\alpha_{\text{solid}}$ for a given solvent to be related to the ratio of the slopes m of the lines passing through the points (k_d/k_c) representing the reaction in the liquid phase and in the solid phase, respectively. Indeed there is nearly a 1:1 correspondence between these quantities, *i.e.*, $\alpha_{\text{liq}}/\alpha_{\text{solid}} \simeq m_{\text{liq}}/m_{\text{solid}}$. This finding augments the validity of our assumption that solvation effects are of negligible importance in this reaction system. It is now clear that the apparent temperature dependence of k_d/k_c in the condensed phases is not a consequence of a conventional thermal effect upon the specific reaction rate whose temperature coefficient is essentially zero. The primary thermal effect is exerted upon the quantity $\delta E/\delta V$ of the solvent and at constant external pressure it manifests itself as a volume change. The spatial requirements of the transition states, relative to that of the reactants, will be more or less readily accommodated by this internal volume change of the medium, depending on the sense of the change, and hence the specific reaction rate will depend on temperature in spite of the fact that its intrinsic temperature dependence is negligible.[20]

We should emphasize the fact that for reactions in the condensed phases the internal volume effect will be invariably present whether the rate process under investigation involves electroneutral, polar, or ionic chemical changes; its importance will depend on the relative magnitudes of the various perturbations which the solvent imposes upon the reacting species. Now we may inquire into the possibility of finding other systems of reactions whose rates at constant temperature may vary with solvent changes in accordance with eq 2. It is to be noted that this equation does not require that the reaction be electroneutral. As we already pointed out, the only requirements are that the activation parameters involved in the solvation term of eq 1 must cancel out, or must not change when the solvent is changed. The volume of activation may be positive, negative, or zero, whereby in the latter case a medium effect may or may not be observed. These activation parameters are thermodynamic excess functions which distribute themselves between the ΔH and the $T\Delta S$ terms of the free energy of activation and for any reaction in solution the heat of activation $\Delta H^{\ddagger}$ will consist of three parts, one of which is an intrinsic property of the reaction, $\Delta H_0^{\ddagger}$, one arising from solvation phenomena, $\Delta H_s^{\ddagger}$, and another contributed from the internal volume effects, *i.e.*

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \Delta H_s^{\ddagger} + \Sigma V_i(P_i^{1/2} - P_s^{1/2})^2 \quad (6)$$

For a strictly electroneutral reaction the solvation parameter, $\Delta H_s^{\ddagger}$, is essentially zero (regular solutions) and for this case eq 6 reduces to

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \Sigma V_i(P_i^{1/2} - P_s^{1/2})^2 \quad (7)$$

from which, depending on the type of reaction investigated, a linear function may be approximated for graphical purposes. For these reaction systems the change in the entropy of activation from solvent to solvent may also be essentially zero, and in that event the factor controlling the variation in the specific reaction rate in a series of solvents is the excess heat of activation which is given by $\Sigma V_i(P_i^{1/2} - P_s^{1/2})^2$. On the other hand, for nonelectroneutral systems both $\Delta S^{\ddagger}$ and $\Delta H_s^{\ddagger}$ may change appreciably as the solvent is changed, but in spite of this, eq 2 may still be applicable at some particular temperature because the free-energy change due to solvation effects may be constant in the solvent series examined, *i.e.*

$$\Delta H_s^{\ddagger} = T\Delta S^{\ddagger} + \text{constant} \quad (8)$$

Equation 8 is analogous to the linear relation, between the logarithm of the PZ factor and the Arrhenius activation energy, discussed by Fairclough and Hinshelwood,[21] and by Evans and Polanyi,[5] and which was subsequently developed by Leffler into the isokinetic relation.[22] Equation 8 differs from the isokinetic relation, however, in that the latter is a linear relation between the experimental heats and entropies of activation whereas in eq 8 the quantities involved are excess functions. By contrast to the isokinetic relation the temperature in eq 8 is not necessarily an isokinetic parameter, but rather it is the temperature at which a given reaction, when studied in different solvents, exhibits a constant free energy of activation throughout the series of solvents and which energy arises from solvation phenomena only. The specific reaction rate will not necessarily be the same in all solvents since the internal volume factor may not be zero. Furthermore, the activation parameters $\Delta H_s^{\ddagger}$ and $\Delta S^{\ddagger}$ of eq 8 are functions of the configurational free energy of the solute–solvent system, and since their magnitudes depend on specific interactions and on the dielectric properties of the system which depend on temperature, they themselves will be functions of temperature. The temperature dependence of the total heat of activation, $\Delta H^{\ddagger}$, will of course be appreciably noticeable only if the

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(20) Actually, with varying temperature this state of affairs is more complicated since the volume of activation is itself a function of temperature.

(21) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937).

(22) J. E. Leffler, *J. Org. Chem.*, 20, 1202 (1955).

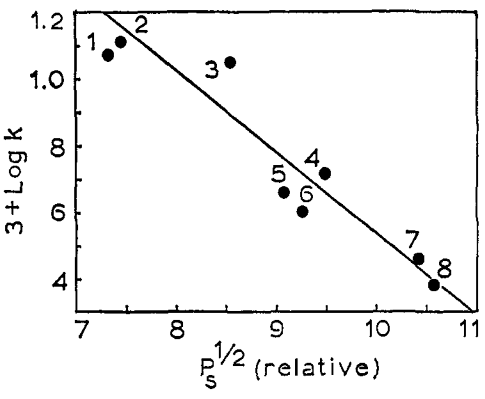

Figure 4. Esterification of ethanol with acetic anhydride in various solvents (ref 8). Log *k vs.* the square root of the internal pressure of the solvent: (1) hexane, (2) heptane, (3) carbon tetrachloride, (4) chlorobenzene, (5) benzene, (6) chloroform, (7) anisole, (8) nitrobenzene.

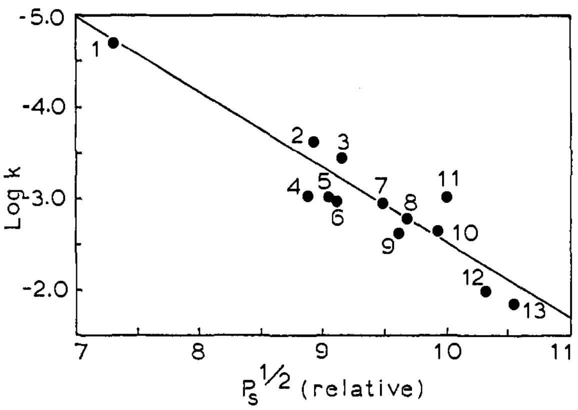

Figure 5. Reaction of triethylamine with ethyl iodide: H. G. Grimm, H. Ruf, and H. Wolf, *Z. Physik. Chem.*, **6**, 41 (1890). Log *k vs.* the square root of the internal pressure of the solvent: (1) hexane, (2) toluene, (3) benzene, (4) diphenylmethane, (5) fluorobenzene, (6) diphenyl ether, (7) chlorobenzene, (8) bromobenzene, (9) acetone, (10) iodobenzene, (11) dioxane, (12) benzonitrile, (13) nitrobenzene.

parts contributed to it by the excess functions $\Delta H_s^{\ne}$ and $\Sigma V_i(P_i^{1/2} - P_s^{1/2})^2$ are of a magnitude comparable to that of the intrinsic heat of activation, and even then the effects of the internal volume function will be discernible only if the changes in the solvation function are not random and also large. Furthermore, if these two excess functions change with temperature in such manner that their respective changes compensate each other or nearly do so, the temperature dependence of $\Delta H^{\ne}$, under the usual working conditions, will be nonobservable or it will be within experimental error. We emphasize here the statement, "under the usual working conditions" since values of $\Delta H^{\ne}$ for reactions in solution are usually determined from a very small number, sometimes only three, of experimental points over a rather narrow, and frequently the same, temperature range. The manifestation of the interplay between $\Delta H_s^{\ne}$ and $\Sigma V_i(P_i^{1/2} - P_s^{1/2})^2$ is suggested by eq 2, 6, and 7 which may be used as a test for it and which, under certain circumstances, will also indicate whether or not a linear relation between $\Delta H^{\ne}$ and $\Delta S^{\ne}$ is random or accidental. The extent to which the medium perturbs the rate process by solvation interactions, and perhaps the nature of these perturbations,

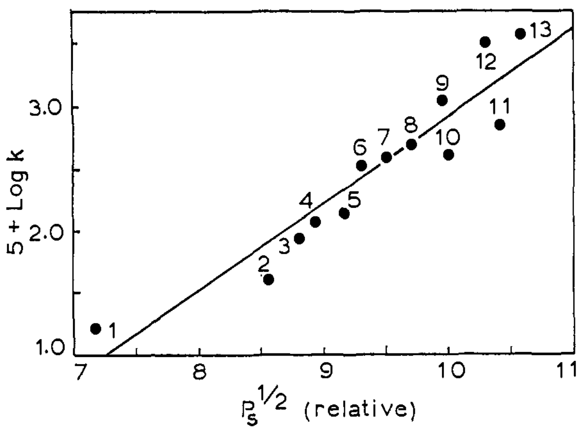

Figure 6. Reaction of pyridine with methyl iodide (ref. 32). Log *k vs.* the square root of the internal pressure of the solvent: (1) isopropyl ether, (2) carbon tetrachloride, (3) mesitylene, (4) toluene, (5) benzene, (6) chloroform, (7) chlorobenzene, (8) bromobenzene, (9) iodobenzene, (10) dioxane, (11) anisole, (12) benzonitrile, (13) nitrobenzene.

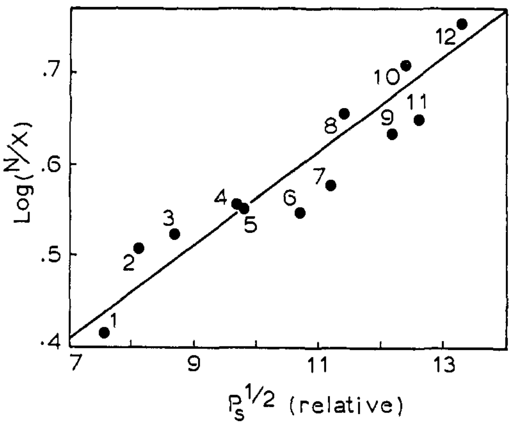

Figure 7. Reaction of methyl acrylate with cyclopentadiene (ref) 33). Log (*N*/*X*) *vs.* the square root of the internal pressure of the solvent: (1) triethylamine, (2) decalin, (3) 1,2-dimethoxyethane, (4) acetone, (5) 1,2-dichloroethane, (6) pyridine, (7) dimethylformamide, (8) ethanol, (9) acetonitrile, (10) acetic acid, (11) nitromethane, (12) methanol.

can be estimated from the deviations of the experimental points from the theoretical curve of the plot of log *k* or of $\Delta H^{\ne}$ *vs.* some function of the cohesive energy density of the solvent. It must be observed, however, that in many systems "the usefulness of internal pressures (solubility parameters) for estimating solute–solvent interactions in solvents such as ethylene glycol, aniline, alcohols, etc., is debatable. The thermodynamic properties of solutes in these solvents cannot be explained this way; it is unreasonable to expect reaction kinetics to fit any better."[23] Some reactions in which a near compensation between the solvation and the internal volume excess functions is evidently operative have been discussed by Hinshelwood[21] and by Leffler and Grunwald,[24] and as examples of this behavior we may cite the esterification of ethanol with acidic anhydride, two variations of the Menschutkin reaction, and two cycloaddition reactions which are illustrated graphically in Figures 4–9. The lines in these figures are not the theoretical curves. It is note-

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(23) Comments of referee.

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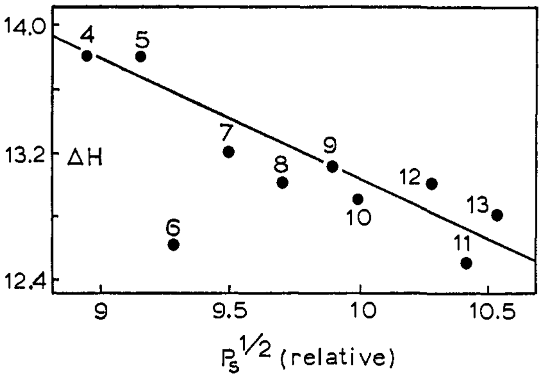

Figure 8. Reaction of pyridine with methyl iodide (ref 32). $\Delta H^{\ddagger}$ *vs.* the square root of the internal pressure of the solvent.

worthy to point out that the internal pressure–log *k* plots in Figures 4 to 7 are far better correlations than those in which log *k* is correlated with the dielectric constant of the medium. Apparently the rates of certain polar reactions correlate well with the dielectric properties of the medium only if the latter is a mixture of different solvents.[21,25] The applicability of eq 2 and 6 to reactions in mixed solvents cannot be tested, however, without measuring the fundamental quantity $(\delta P/\delta T)$ for the different solvent mixtures. A check of several other polar reactions randomly selected from the literature showed that nearly all of the systems checked conformed to the foregoing considerations, and as we already explained deviations of the experimental points from the theoretical curves are understandable. Some of these reactions are the following: decomposition of benzoyl azide,[26] reaction of aniline with phenacyl bromide,[27] decomposition of *t*-butoxy radicals,[28] decomposition of nitrogen pentoxide,[29] racemization of the dimethyl ester of 2,2′-dimethoxy-6-6′-dicarboxydiphenyl,[30] decomposition of phenylazotriphenylmethane,[31] benzoylation of *m*-nitroaniline,[32] reaction of cyclopentadiene with methyl methacrylate and with methyl *trans*-crotonate.[33]

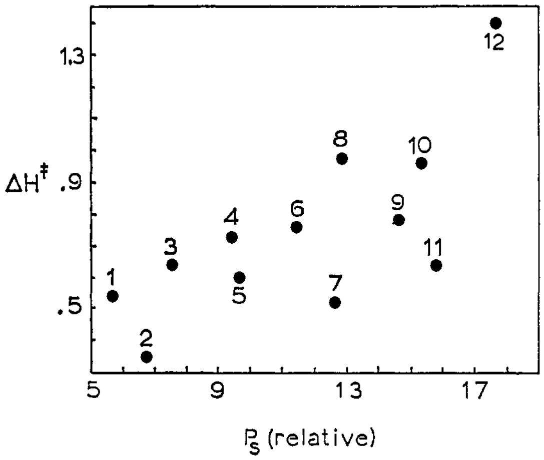

Figure 9. Reaction of methyl acrylate with cyclopentadiene (ref 33). $\Delta H^{\ddagger}$ *vs.* the square root of the internal pressure of the solvent.

Acknowledgments. This work was supported by the National Science Foundation, the American Chemical Society Petroleum Research Fund, and the Research Corporation. We gratefully acknowledge this support.

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Charge-Transfer Intensities of Iodine Complexes with N-Heterocyclics[1a]

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Abstract: The oscillator strengths of charge-transfer bands in the molecular complexes of iodine with six pyridines and four quinolines are shown to increase with the heats of formation in agreement with Mulliken's previous prediction. An empirical method of obtaining dissociation energies of iodine complexes is described.

Our present knowledge of the relationships between the stability of the charge-transfer (CT) complexes and their transition probability is in an unsatisfactory state, even though such knowledge is of central importance in the CT theory for the following reason.[2,3] The usage of the term CT complex implies that the

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[1] (a) Supported in part by Grant GM-1422 from National Institutes of Health. Part of the work by V. G. K. was done during 1964–1965 at the Institute of Molecular Biophysics, Florida State University, Tallahassee, Fla., and supported by Division of Biology and Medicine of the U. S. Atomic Energy Commission. (b) Department of Chemistry, University of Arizona, Tucson, Ariz. 85721.

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