importance in determining the equilibrium ionic distribution as the degree of cross-linking of the resin is increased. Conversely, if there is essentially no cross-linking, as for linear polyelectrolytes, it might be expected that the free energy of exchange would approximate that to be expected from the Debye–Hückel treatment of electrolytes in solution, since the limitation of motion of the cations resulting from volume available within the pores of the resin no longer would be a governing factor.

Thus, it might be expected that this treatment in its present form would describe most nearly the ionic distribution for exchanges involving moderately cross-linked resins and cations whose sizes are not such as to make their ability to diffuse through the resin pores the controlling factor in determining their equilibrium distribution.

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The Role of the Solvent in Radical Decomposition Reactions: Phenylazotriphenylmethane

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A well-known property of radical dissociation reactions is insensitivity of the rate to changes in solvent. However, the insensitivity of the rate is not necessarily due to absence of strong interaction between the solvent and either the starting or transition states. In the present example there is an important interaction with the solvent and the small effect on the rates is due to simultaneous large but compensating changes in enthalpy and entropy of activation.

Introduction

The insensitivity of the rates of radical decomposition reactions to changes in solvents has usually been considered to be the result either of complete absence of interaction of the reagents with the solvent or of equivalent interaction of the solvent with both the ground and transition states of the reagent. The comparative rarity of ideal mixtures makes the former explanation implausible. On the other hand, it is hard to believe that all radical dissociation transition states should be solvated to exactly the same extent as their ground states. Some differences in electronic configuration and polarizability should exist. In the case of aromatic systems, the formation of complexes[3] with the reagent should put partial charges on the reagent molecule. These should affect the bond strength in much the same way as a substituent. Unless the average solvation state of the reagent molecules happens to coincide with the one corresponding to the lowest strength of the bond to be broken, there should be a change in solvation on attaining the transition state. We now present evidence for such an effect in the decomposition of phenylazotriphenylmethane in a series of solvents.

Experimental

Phenylazotriphenylmethane was synthesized by the method of Gomberg and Berger.[4] Crystallization from ether gave material melting with decomposition at 111–113°. The decomposition temperature is not sensitive to the presence of the hydrazo compound in small amounts. The hydrazo compound may be removed by shaking with lead dioxide until no further increase in optical absorption is observed. The absorption spectrum was similar in all five solvents. The consistent band maximum at 420 mμ agrees well with that at 420.5 mμ reported by Burawoy using hexane as a solvent.[5] The optical extinction at this wave length was used in following the decomposition of the azo compound.

All of the solvents used were freshly distilled. Samples of the solutions were outgassed and sealed in ampoules under one atmosphere of nitrogen and kept frozen in Dry Ice–acetone until used. The kinetic measurements were made by placing the sealed ampoules in thermostated baths (±0.02°). At the end of a measured time interval, the ampoule was removed, quenched in Dry Ice–acetone, warmed to room temperature, opened, and the optical density of the contents measured at 420 mμ. Because variations in the optical analysis, in the degassing and sealing procedure, and in the amount of colored by-products, made it impossible to obtain high precision in the rate constants, these were determined over a very wide temperature range to obtain sufficiently precise activation parameters. Each rate constant represents a considerable number of separate experiments, a different degassed ampoule being used for each time interval and at least two initial concentrations being represented. The colored by-product amounted to less than 10% of the initial optical density and was corrected for by using an equation 1 derived from the assumption that the colored by-product was formed continuously. The same equation may be derived if the assumption is made that the by-product was all present at the beginning of the run.

$$\log \frac{(\epsilon_A - \epsilon_B')[A]_0}{2.30D - \epsilon_B'[A]_0} = \frac{kt}{2.30} \qquad (1)$$

$$\epsilon'_B = \frac{2.30D_\infty}{[A]_0} \qquad (2)$$

where

$[A]_0$ = initial concn. of phenylazotriphenylmethane
ϵ_A = extinction coeff. of phenylazotriphenylmethane
D = optical density at time t
t = time in seconds
k = first-order rate constant, sec.$^{-1}$
ϵ_B' = a pseudo-extinction coeff. for the impurity responsible for the infinity color
D_∞ = the optical density at infinite time

Figure 1 illustrates the application of equation 1 to the data for the decomposition of phenylazotriphenylmethane in

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[1] (1) Office of Naval Research Post-doctoral Research Associate, 1951–1952.

[2] (2) To whom requests for reprints should be addressed.

[3] (3) Note for example the contribution of ionic structures to the wave functions of molecular complexes: R. S. Mulliken, This Journal, **74**, 811 (1952).

[4] (4) M. Gomberg and H. W. Berger, *Ber.*, **36**, 1088 (1903).

[5] (5) A. Burawoy, *J. Chem. Soc.*, 1865 (1937).

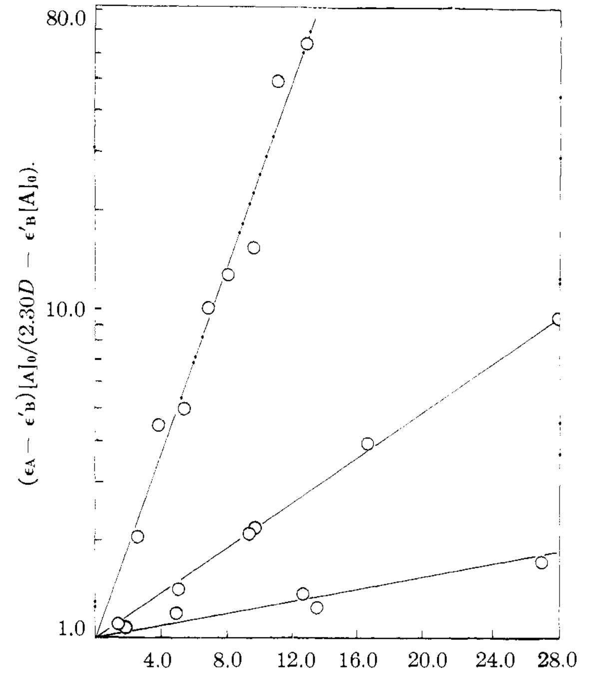

Fig. 1.—First-order dependence of the thermal decomposition of phenylazotriphenylmethane: top line, 348°K., $[A]_0 = 2.65 \times 10^{-3}$ *M*, total abscissa range 2800 sec.; middle line, 323°K., $[A]_0 = 4.02 \times 10^{-3}$ *M*, total abscissa range = 280 min.; bottom line, 298°K., $[A]_0 = 2.99 \times 10^{-3}$ *M*, total abscissa range 2800 min.

benzene. A similar first-order dependence occurs in all five solvents. A summary of the rate constants is given in Table I, the activation parameters in Table II.[6]

A product analysis of the decomposition of phenylazotriphenylmethane gave results similar to those reported earlier, consistent with the production of free radicals.[7,8] The decomposition in styrene, which proceeds at about the same rate as in other solvents, initiates the polymerization of the styrene.[9]

Discussion

In order to assess the role of the solvent in the reaction, enthalpies and entropies of activation, together with their probable errors, were calculated by the method of least squares. It will be noted that the spread in values of both $\Delta H^\ddagger$ and ΔS^* for the various solvents is much greater than the probable errors involved. The apparent indifference of the rate to solvent change is thus due to the compensating direction of the enthalpy and entropy changes and to the fact that the temperature range in which the rates were measured includes the temperature at which the rates will be exactly equal in all solvents. This temperature, 36°, can be calculated from the empirical relationship observed between $\Delta H^\ddagger$ and ΔS^*. The free energy of activation is therefore nearly constant. Were it not for the compensating effect of the entropy of activation, the 4.5 kcal. change in $\Delta H^\ddagger$ in going from cyclohexane to benzonitrile as solvent, would product a rate ratio of about 500 instead of the observed value near 1.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE

Temp., °K.	[A], moles/l. (10³)	Number of individual detns.	*k* in sec.⁻¹
	Solvent, benzonitrile		
298.3	2.88	3	2.71×10^{-6}
298.3	1.39	1	2.37×10^{-6}
323.6	2.78	3	1.38×10^{-4}
323.6	1.25	3	1.73×10^{-4}
348.0	2.45	3	3.14×10^{-3}
	Solvent, anisole		
298.3	3.91	3	3.04×10^{-6}
298.3	3.19	2	1.88×10^{-6}
323.5	3.81	5	1.43×10^{-4}
323.5	3.03	3	1.10×10^{-4}
348.0	3.23	4	3.10×10^{-3}
348.0	2.98	4	2.95×10^{-3}
298.2[a]			2.96×10^{-6}
	Solvent, chlorobenzene		
298.3	0.798	2	3.56×10^{-6}
298.3	2.48	2	3.97×10^{-6}
322.9	0.778	2	1.66×10^{-4}
322.9	2.36	3	1.67×10^{-4}
348.0	0.738	2	3.71×10^{-3}
348.0	1.66	3	4.07×10^{-3}
	Solvent, benzene		
298.3	4.06	2	4.10×10^{-6}
298.3	2.99	5	4.37×10^{-6}
322.9	4.02	7	1.24×10^{-4}
348.0	3.70	4	2.84×10^{-3}
348.0	2.65	8	3.26×10^{-3}
298.2[a]			3.09×10^{-6}
	Solvent, cyclohexane		
298.3	1.24	6	4.22×10^{-6}
322.9	1.00	3	0.860×10^{-4}
322.9	1.07	3	0.920×10^{-4}
322.9	2.62	5	1.11×10^{-4}
348.0	0.791	5	1.93×10^{-3}
348.0	2.59	4	1.69×10^{-3}
348.0	2.63	4	1.59×10^{-3}

[a] The diphenylpicrylhydrazyl data.[6]

TABLE II

ACTIVATION PARAMETERS FOR THE UNIMOLECULAR DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE

Solvent	$\Delta H^\ddagger$, kcal./mole	ΔS^*, cal./deg.
Benzonitrile	29.0 ± 0.3	13.4 ± 0.9
Anisole	28.8 ± 0.2	12.5 ± 0.7
	28.3 ± .3[a]	11.0 ± .9
Chlorobenzene	28.3 ± .1	11.4 ± .4
Nitrobenzene	28.4 ± .25[a]	11.2 ± .8[a]
Malonic ester	27.9 ± .15[a]	9.7 ± .4[a]
Benzene	26.8 ± .1	6.57 ± .3
Cyclohexane	24.5 ± .1	−1.16 ± .4

[a] Data from nitrogen evolution and diphenylpicrylhydrazyl methods.[6]

Figure 2 shows that the increment in $\Delta H^\ddagger$ is proportional to the increment in ΔS^*. Since the

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(6) The data marked with an superscript *a* in Tables I and II and in Fig. 2 are based on unpublished work with R. A. Hubbard, II, using the nitrogen evolution and diphenylpicrylhydrazyl methods. The latter is a direct measure of the rate of production of free radicals, but is interfered with by traces of oxygen.

(7) H. Wieland, E. Popper and H. Seefried, *Ber.*, **55**, 1816 (1922).

(8) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

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process of desolvation of the starting state is roughly analogous to the process of separation of a solute molecule from its crystal lattice during solution, it is not surprising that a similar linear relationship has been noted for the enthalpies and entropies of solution into saturated solutions for a wide range of solid solutes.[10] It is also pertinent that the order of increasing enthalpy of activation is that to be expected for the order of increasing stability of the solvent complexes. The increase in enthalpy of activation from cyclohexane to the aromatic solvents is of the same order of magnitude as the heat of solvation of benzene in nitrobenzene: 3.1 kcal./mole.[11] Table III shows the parallelism between the entropies of activation and the entropies of fusion of three of the solvents used. These facts strongly suggest that the process of activation involves desolvation.

TABLE III

THE UNIMOLECULAR DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE. A COMPARISON OF THE ENTROPY OF ACTIVATION OF THE SOLUTE WITH THE ENTROPY OF FUSION OF THE SOLVENT

Solvent	ΔS^*, cal./deg.	ΔS_f, cal./deg.
Chlorobenzene	11.4 ± 0.4	10.2
Nitrobenzene	11.2 ± .8	9.9
Benzene	6.57 ± .3	7.86
Cyclohexane	−1.16 ± .4	2.25

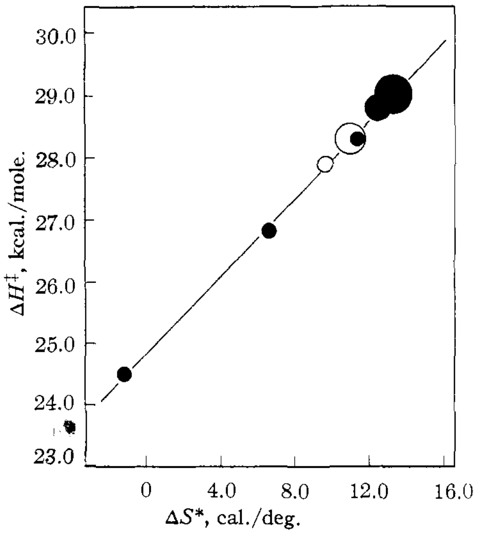

Fig. 2.—Activation parameters for the decomposition of phenylazotriphenylmethane in various solvents. The open circles are nitrobenzene and malonic ester.

The Radical Dissociation of Ethanes.—The rates of dissociation of hexaphenylethane in a series of 28 solvents were found by Ziegler and his co-workers to vary by less than a factor of four. But, unlike the case of phenylazotriphenylmethane, the activation energies were substantially constant and the entropies small: the indifference of the rate to solvent changes was due not to compensation but to a genuine lack of participation by the solvent. It will be noted that hexaphenylethane is sterically hindered in solvation and that the transition state for the dissociation will resemble the ground state closely and hence will also be sterically hindered.[12] When the crowding in hexaphenylethane was reduced by replacing two of the phenyl groups with methyl groups, Ziegler's data showed a large positive entropy of activation for the dissociation in bromobenzene. This was somewhat reduced when the methyl groups were in turn replaced by branched alkyl groups and the reduction was of the same order of magnitude as the entropy of activation of phenylazotriphenylmethane in aromatic solvents.

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[10] M. G. Evans, *Trans. Faraday Soc.*, **32**, 1333 (1936); **33**, 166 (1937). See also A. E. Remick, "Electronic Aspects of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 347 ff.

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

[12] J. E. Leffler, *Science*, **117**, 340 (1953).