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THE EFFECT OF COMPLEXING IN RADICAL DECOMPOSITION REACTIONS

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INTRODUCTION

Since the enthalpy and entropy of complexed molecules will in general differ from those of uncomplexed molecules, a complexing agent can affect the enthalpy and entropy of activation of a reaction. The free energy of activation, which determines the rate,[2] may not be changed by the complexing agent if the temperature happens to be such that the change in entropy multiplied by the absolute temperature exactly compensates for the change in enthalpy of activation. Assuming that there is no exact compensation of the enthalpy and entropy changes, a complexing agent may either accelerate or decelerate a reaction.

A reaction will be slowed down by a complexing agent if the complexing agent is associated with the initial state of the reagent to a greater degree than with the transition state. The free energy of the initial state is reduced, thus increasing the free energy of activation needed to attain the transition state. We need not consider the case that the standard free energy of the complexed initial state molecules is increased since such a complex will be highly dissociated and the initial state will be the same as in the absence of the complexing agent. Nor do we need consider the case that the complexed transition state has a higher free energy than the uncomplexed transition state, since the reaction will avoid such a path. Because the reaction will be slowed down only to the extent that the complexed initial state exists as such and not dissociated into its components, such an effect will be detectable only in favorable cases. It should be detectable when the complexing agent is one that forms unusually stable complexes or when it is present in very high concentrations or as the solvent.

A reaction will be accelerated by a complexing agent if the complexing agent is associated with the transition state of the reagent more than with the initial state. We can expect this if the transition state contains stronger internal dipoles or if the transition state is more polarizable than the initial state. The reason that the transition state of even a radical reaction might contain stronger internal dipoles derives from the influence of electronegativity on bond strength. It has been shown that, other things being equal, a bond is weakest when the bonded groups are most nearly equal in electronegativity (1). It is reasonable to assume that the contribution of resonance structures corresponding to electron

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[2] $k = \frac{\bar{k}T}{h} e^{-\Delta H\ddagger/RT} e^{\Delta S\ddagger/R} = \frac{\bar{k}T}{h} e^{-\Delta F\ddagger/RT}$

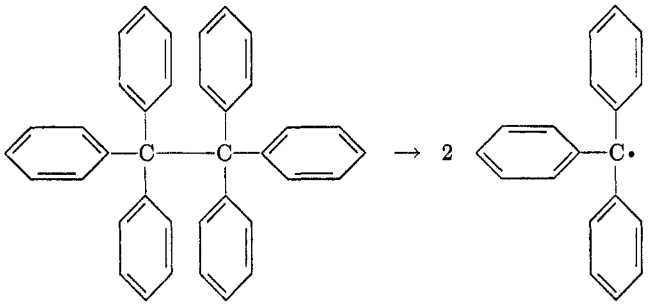
release and withdrawal is adjusted in the transition state to bring about a closer approach to equal electronegativity of the bonded atoms. Such an electronic shift will either increase or decrease the complexing power of the transition state. The same prediction may be reached from another point of view. It is known that the wave function of molecular complexes includes a charge-transfer term, thus making the complexed substrate more or less electronegative than the uncomplexed substrate (2). There will be some one "solvation state" or "complexing state" corresponding to most nearly equal electronegativity of the two bonded groups. Only rarely should this be the state in which both groups are completely unsolvated.

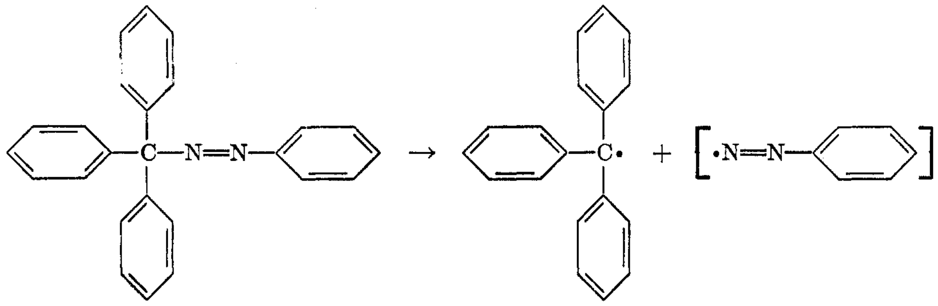
We can also expect acceleration by the complexing agent if there is any important degree of resemblance between the transition state of the radical decomposition reaction and the radicals produced. The radicals produced will have a resonance-stabilized structure as nearly planar as the steric requirements allow. They should resemble a large polynuclear aromatic hydrocarbon in their ability to form complexes. The large variation in the equilibrium constant for the dissociation of hexaphenylethane in various solvents (3) is probably due to the fact that whereas the sterically hindered ethane is largely unsolvated, the triphenylmethyl free radical is solvated (complexed) to a degree that varies strongly with the solvent. Whether or not the rate will be increased by complexing agents or changes to solvents of superior complexing power depends on how much the transition state resembles the radicals rather than the starting material, both geometrically and in polarizability.

DISCUSSION

We have chosen two types of radical decomposition reaction for study. One of these, the dissociation of hexaphenylethanes, might be expected to be accelerated by symmetrical complexing of both triphenylmethyl groups in the transition state. The other, the decomposition of phenylazotriphenylmethane, might be expected to be decelerated by complexing agents, since another study of the decomposition in a series of solvents has indicated that the azocompound, initially solvated, releases solvent on passing to the transition state. The sequence of the solvent effects is what might be expected on the basis of the complexing ability of the solvents (4). As a complexing agent we have chosen *sym*-trinitrobenzene.

The dissociation of hexaphenylethane was studied by an oxygen-absorption method similar to that of Ziegler (3) using pyrogallol as a chain-breaking agent. The rate constants obtained in diethyl malonate (chosen because it is a good solvent for trinitrobenzene) are tabulated for various concentrations of trinitrobenzene in Table I. The effect of the trinitrobenzene is an acceleration, but too small to be of definite significance in view of the relatively large scatter in the rate constants obtained by this method. A similarly small, or entirely negligible, acceleration was noted (Table II) in the case of 1,2-di(*p*-methoxyphenyl)-tetraphenylethane, chosen for the electron-releasing effect of the methoxyl group, favorable to complexing with trinitrobenzene. The small change in rate





constant with solvent observed by Ziegler together with the constant enthalpy of activation in a series of solvents suggests that *both* the initial and transition states of hexaphenylethane are very little solvated. This is in contrast to the large change in equilibrium constant corresponding to the different degrees of solvation of the free radical in various solvents. The extrathermodynamic relationship observable between Ziegler's rate and equilibrium constants leads to a quantitative description of the transition state as resembling the ethane about four times as much as it does the radicals (5). The small or insignificant acceleration observed here confirms the picture of the transition state as resembling the sterically-hindered initial state. Apparently the effect of the trinitrobenzene is insufficient to convert the transition state from that characteristic of the usual solvents to one more nearly resembling the free radicals. It should be noted that both the resonance-stabilized triphenylmethyl radical and the symmetrical trinitrobenzene have three-fold axes of symmetry so that a symmetrical structure would be possible for the complex.

The decomposition of phenylazotriphenylmethane was followed by measuring the pressure of the evolved nitrogen. The rate constants are given in Table III and the least square activation parameters together with their probable errors in Table IV. To increase the significance of the activation parameters the nitrogen evolution data taken over a narrow temperature range were supplemented with measurements by the diphenylpicrylhydrazyl method at a much lower temperature (6). It has been found that both of these methods give results in agreement with those obtained by the ultraviolet spectrophotometric method where a comparison is possible (4). The effect of the trinitrobenzene is to increase the activation enthalpy of the decomposition, but only by about four

TABLE I

SUMMARY OF DATA OBTAINED FOR HEXAPHENYLETHANE

CONCENTRATION OF *sym*-TRINITROBENZENE, molarity	FIRST ORDER RATE CONSTANT for oxygen absorption, sec^{-1}, at —8.56°[a]
0.0	6.6
.022	7.5
.022	7.5
.052	7.6
.052	7.7
.056	7.2
.058	8.6
.057	8.3
.189	9.0
.186	9.3
.202	7.6
.202	8.2
.191	7.7
.150	8.6
.150	9.3

[a] Twice that for the dissociation of the ethane.

TABLE II

SUMMARY OF DATA OBTAINED FOR 1,2-DI(*p*-METHOXYPHENYL)TETRAPHENYLETHANE

PARTIAL PRESSURE OF OXYGEN, atm.	CONCENTRATION OF *sym*-TRINITROBENZENE, moles/liter	FIRST ORDER RATE CONSTANT for oxygen absorption,[a] sec ^{1} k × 10^{3}
0.2	0	2.11
.2	0	2.16
.2	0	2.25
		Avg. 2.17
.2	0.15	2.25
.2	.14	2.78
.2	.15	2.39
		Avg. 2.47
1.0	0	2.52
1.0	0	2.54
		Avg. 2.53
1.0	.13	2.46
1.0	.15	2.60
		Avg. 2.53

[a] Twice that for the dissociation of the ethane.

times the probable error. Such an effect is consistent with the solvent-variation data and suggests a partially complexed initial state and an uncomplexed transition state.

EXPERIMENTAL

Hexaphenylethane. The hexaphenylethane was prepared on a vacuum bench from triphenylmethyl chloride and silver in the solvent used in the dissociation experiments. After outgassing the trityl chloride solution, mercury was added by rotating a side arm

TABLE III
Decomposition of Phenylazotriphenylmethane

SOLVENT	TEMP., °C.	INITIAL MOLARITY AT ROOM TEMP. $(\times 10^2)$	RATE CONSTANT sec^{-1}
Nitrobenzene	74.50[a]	1.49	3.0×10^{-3}
		0.45	3.1
		2.49	2.9
		1.84	3.0
	80.09[a]	1.00	5.3
		1.63	5.4
		2.81	6.4
		2.06	6.1
		1.16	6.2
		.55	6.0
		1.56	5.9
		1.36	5.1
	85.87[a]	2.16	9.8
		1.48	9.5
		4.77	9.9
	25.05[b]	.220	2.5×10^{-6}
		.272	2.7×10^{-6}
Anisole	74.50[a]	1.88	2.87×10^{-3}
		.81	2.90
		2.84	3.03
	80.09[a]	3.05	6.5
		1.22	6.9
		1.31	6.8
		1.73	6.6
		4.06	6.7
		5.15	6.8
		.51	6.9
		1.17	6.9
	85.87[a]	1.07	10.7
		1.78	11.3
		6.85	10.8
		3.72	11.1
	25.00[b]	.232	2.92×10^{-6}
		.232	2.96×10^{-6}
		.294	2.99×10^{-6}
Diethyl malonate	74.50[a]	1.24	2.72×10^{-3}
		.76	2.84
		.60	2.78
		.62	2.83
		1.57	2.83
	80.09[a]	1.12	6.6
		2.68	4.7
		1.64	6.5
		2.19	5.7
		3.23	5.6
		4.01	6.0
		.89	6.6
	85.87[a]	7.00	10.1
		4.33	10.2
		1.91	10.5
	25.15[b]	.237	3.11×10^{-6}
	25.10[b]	.232	3.08×10^{-6}

TABLE III—*Continued*

SOLVENT	TEMP., °C.	INITIAL MOLARITY AT ROOM TEMP. ($\times 10^{-2}$)	RATE CONSTANT sec^{-1}
Diethyl malonate with 0.0363 mole-fraction of *sym*-trinitrobenzene	74.50[a]	1.38	3.3×10^{-3}
		1.15	3.3
		.47	3.1
		2.66	2.9
		2.34	2.7
	80.09[a]	1.56	6.0
		1.95	6.0
		.89	6.3
		.62	5.6
		1.30	6.1
		1.29	5.9
		3.02	6.5
	85.87[a]	.91	10.4
		2.60	10.8
		5.09	9.6
	25.05[b]	.276	2.26×10^{-6}
Diethyl malonate with 0.0195 mole-fraction of *sym*-trinitrobenzene	74.50[a]	.99	3.4×10^{-3}
		1.53	3.2
		1.01	2.9
		1.23	3.1
		1.33	3.3
		1.07	3.1
Diethyl malonate with 0.0159 mole-fraction of *sym*-trinitrobenzene	80.09[a]	1.44	5.8×10^{-3}
		1.73	5.8
		.96	5.8
		2.36	5.9
		5.45	6.1
		4.90	5.5
		.55	6.1
		.67	6.0

[a] By the nitrogen method. [b] By the diphenylpicrylhydrazyl method.

TABLE IV

ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE

SOLVENT	$\Delta H\ddagger$ kcal/mole	$\Delta S\ddagger$ cal/deg
Anisole	28.28 ± 0.30	11.04 ± 0.89
Nitrobenzene	28.38 ± .25	11.16 ± .76
Diethyl malonate	27.86 ± .15	9.69 ± .44
Diethyl malonate with 0.0363 mole fraction of *sym*-trinitrobenzene	29.1 ± .3	13.3 ± .8

and the mixture was stirred magnetically for at least one hour to insure complete reduction of the trityl chloride at room temperature. The hexaphenylethane solution was then pumped by pressure of pre-purified nitrogen through a sintered glass filter and into an evacuated ampoule-filling device containing capillary tubes terminating in thin-walled glass bulbs. When sufficient hexaphenylethane solution was present in the filling device, nitrogen was admitted to force the solution into the ampoules which were then removed and sealed in a flame. The ampoules were weighed before and after filling to get some idea of the amount of ethane used in a run. The filled ampoules were stored in a brown bottle to reduce photochemical disproportionation.

The *diethyl malonate* was distilled at atmospheric pressure, keeping a middle fraction of constant boiling point. *Trinitrobenzene*, Eastman White Label, was purified according to the directions of Jones and Neuworth (6) (m.p. 123.5–123.6°). The *trityl chloride* was purified by several recrystallizations from a mixture of acetyl chloride and petroleum ether.

The kinetic apparatus finally developed consisted of a round flask with a small depression in the bottom to hold the ampoule of hexaphenylethane solution. Solvent was added and the apparatus was assembled and placed in the $-8.56°$ thermostat, and connected to a differential manometer. The other arm of the differential manometer was connected to a flask containing pure solvent in the same thermostat to minimize the effect of any drift in temperature which might occur during a run. The flask was agitated by a shaking device, glass springs being used for the connection to the manometer. Two traps in series prevented solution from splashing into the spring and interfering with the smooth flow of oxygen. A baffle helped minimize transfer of solution into the traps. The reaction with the oxygen (air) in the system was started by crushing the hexaphenylethane ampoule with a glass rod. At the end of the crushing stroke a standard taper joint at the upper end of the rod became seated and sealed the apparatus.

The initial uncertainty in time is estimated to be less than 0.5 second. The time error due to the visual reading of the manometer may be as much as 0.7 mm. in the faster early part of a run. Moisture in the air was removed by calcium chloride in some of the runs, but did not seem to affect the rate constants. The reading lens was designed to make the parallax error of the manometer cancel out between readings; it is important only in the latter part of a run when the timing error is relatively small. The manometer fluid was ethyl anisate colored with Gentian Violet and containing Dow Antifoam A to reduce surface tension. Lag experiments indicate that the manometer kept up with the pressure changes after the first two or three minutes and that the error due to lag in the early readings is less than 0.1 mm.

An important source of error is in the infinity value of the pressure change; some reaction caused a slow absorption of gas from the system after the run. This reaction may be oxidation of the pyrogallol in spite of the presence of added benzoic acid. The reported rate constants are corrected for this error by a method of successive approximations to the infinity reading. The true infinity-reading was taken as that which gave the same rate constant when applied to a set of points near the middle of the reaction as when applied to a set of points near the end of the reaction (after three half-lives). The final plots obtained using the corrected infinity-reading were far better straight lines than the initial plots. A typical infinity-reading is 12 to 16 cm. of ethyl anisate. The concentrations of ethane were all of the order of magnitude of 1/1000 *molar*, but varied by about a factor of two from run to run. The rate constants were calculated by the method of least squares.

1,2-Di(p-methoxyphenyl)tetraphenylethane. The same apparatus and method was used as in the case of hexaphenylethane. However, this compound differs from hexaphenylethane in that the rate of oxygen uptake does not become independent of oxygen pressure at 0.2 atmosphere. Experiments were therefore done at 1 atmosphere of oxygen to reduce the error due to a too slow reaction of the oxygen with the radicals. The *p-methoxyphenyldiphenylmethyl chloride* was prepared from the corresponding alcohol by treatment with acetyl chloride. The chloride, purified by three crystallizations from a mixture of acetyl chloride and petroleum ether, melted at 121–122° (7).

Phenylazotriphenylmethane. Phenylazotriphenylmethane was prepared by the method of Wieland (8). Its purity was checked by comparison of the ultraviolet and visible spectra with those obtained by Alder and Leffler, the melting point being insensitive to admixture of phenylhydrazotriphenylmethane (4). The decomposition was followed at temperatures in the range 75 to 85° by measuring the pressure of the evolved nitrogen. The reaction flask was vigorously stirred magnetically while connected to a differential manometer located outside of the bath. The solvent was saturated with nitrogen before the run. The other arm of the differential manometer was connected to a flask containing solvent only and thermostated in the same bath. The connections from the flasks to the manometer led through a reflux condenser. To insure equivalence, the condenser was constructed with both vapor paths in the same jacket in concentric glass spirals. The sample, weighed in a small glass bucket, was suspended in the nitrogen-flushed apparatus by a hook mounted on a standard taper joint. After introduction of the solvent and flushing with nitrogen, the run was started by turning the joint carrying the sample bucket, dropping the sample bucket into the stirred solvent. In some runs it was necessary to use a corrected infinity reading of the manometer, as described for the oxygen absorption experiments.

Because the nitrogen evolution method was not sufficiently precise for activation parameters in the narrow temperature range used, it was supplemented by some determinations of the rate of radical production at 25°, using the method of Bawn and Mellish (9). The latter method is based on the bleaching of the highly colored radical diphenylpicrylhydrazyl on reaction with free radicals. It was found that oxygen interferes, possibly because trityl radicals react too slowly with the diphenylpicrylhydrazyl radical. The ampoules were therefore carefully degassed on a vacuum bench by alternate freezing and pumping. Another complication is due to the drift that occurs in most solvents and which must be measured and applied as a blank correction. This drift can be reduced in some cases by careful purification of the solvent, but remained quite serious in the case of trinitrobenzene in diethyl malonate.

SUMMARY

The effect of trinitrobenzene on the decomposition of hexaphenylethane, 1,2-di(*p*-methoxyphenyl)tetraphenylethane, and phenylazotriphenylmethane is small and consistent with previous descriptions of the transition states of these reactions.

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REFERENCES

(1) GORIN, KAUZMANN, WALTER, AND EYRING, *J. Chem. Phys.*, **7**, 633 (1939).
(2) MULLIKEN, *J. Am. Chem. Soc.*, **74**, 811 (1952).
(3) ZIEGLER AND EWALD, *Ann.*, **473**, 163 (1929).
(4) ALDER AND LEFFLER, *J. Am. Chem. Soc.*, **76**, 1425 (1954).
(5) LEFFLER, *Science*, **117**, 340 (1953).
(6) JONES AND NEUWORTH, *J. Am. Chem. Soc.*, **66**, 1497 (1944).
(7) GOMBERG AND BUCKLER, *J. Am. Chem. Soc.*, **45**, 207 (1923).
(8) WEILAND, POPPER, AND SEEFRIED, *Ber.*, **55**, 1816 (1922).
(9) BAWN AND MELLISH, *Trans. Faraday Soc.*, **47**, 1216 (1951).