

keto-3''-phenyl-5''-thiazolidylmethylenerhodanine) as a red solid, m.p. 197° dec.

Anal. Calcd. for C₂₈H₁₉N₄O₄S₂: N, 7.7; S, 35.2. Found: N, 7.7; S, 34.7.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Role of the Solvent in Radical Decomposition Reactions: *p*-Nitrophenylazotris-(*p*-anisyl)-methane

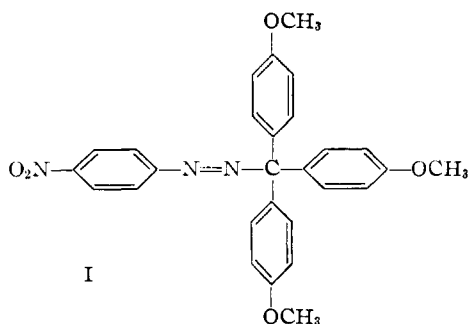
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The decomposition of *p*-nitrophenylazotris-(*p*-anisyl)-methane has been studied in a series of solvents at several temperatures. The changes observed in the activation parameters can be explained in terms of differential solvation of the initial and transition states. In spite of the highly asymmetrical structure of this compound, there appears to be no shift to a polar mechanism in the solvents studied.

Introduction

The decomposition of *p*-nitrophenylazotris-(*p*-anisyl)-methane (I) is of twofold theoretical interest. The substituents present in this molecule should make its interaction with the solvent different from that of phenylazotriphenylmethane⁴ and thus afford a test of the complexing theory of special solvent effects. The polar nature of the substituents might, but apparently did not, shift the mechanism from a radical to a polar one.⁵ The decomposition therefore helps to locate the structural boundaries separating radical from polar mechanisms.



Interpretation of the Results

The decomposition of the azo compound has been followed by the change in pressure of the nitrogen evolved. The rate constants are presented in Table I and the activation parameters in Table II. The trend in activation enthalpies does not parallel that expected for the enthalpies of complex formation of the solvent with the azo compound. This is in contrast to the behavior of phenylazotriphenylmethane, whose enthalpy of activation appeared to include the enthalpy necessary to remove solvent from the solvated ground state molecules.⁴ Nor is there any parallelism between the activation parameters and the solubility of the substituted azo compound. The solubilities will also be found in Table II.

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(4) M. G. Alder and J. E. Leffler, *THIS JOURNAL*, **76**, 1425 (1954).

(5) J. E. Leffler, *ibid.*, **72**, 67 (1950).

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF *p*-NITROPHENYLAZOTRIS-(*p*-ANISYL)-METHANE IN VARIOUS SOLVENTS

Temp., °K.	Benzonitrile		Benzonitrile-veratrole ^c		Decalin		Veratrole	
	C ₀ ^a	k ^b	C ₀ ^a	k ^b	C ₀ ^a	k ^b	C ₀ ^a	k ^b
360.31	5.32	304	2.71	267	4.37	241	3.11	284
	2.61	296	5.38	267	1.86	232	4.41	291
	3.81	288			3.75	223		
	4.16	290			1.84	232		
350.76	2.65	100.8	3.83	87.5	2.77	73.8	3.33	89.6
	2.01	104.1	4.55	90.1	2.94	73.3	3.33	93.7
	5.36	104.8	3.66	94.6	1.93	74.0	5.11	87.9
	4.39	101.4	4.33	90.0	3.23	75.1	4.02	88.1
335.08	5.53	14.0	4.35	13.0	1.96	9.96	3.35	12.25
	4.16	15.7	3.15	13.2	3.85	8.77	3.13	11.33
	1.73	14.6	5.96	12.3	4.78	10.63	4.08	9.91
	3.69	14.4	5.61	12.4	4.43	9.08	3.75	12.64
				2.33	10.82	1.30	11.26	
						4.18	10.67	

^a Initial concentration in moles/liter times 10³. ^b Rate constant in sec.⁻¹ times 10⁵. ^c 49.4% benzonitrile by weight.

TABLE II

SOLUBILITIES AND ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF *p*-NITROPHENYLAZOTRIS-(*p*-ANISYL)-METHANE

Solvent	Enthalpy of activation, kcal./mole	Entropy of activation, cal./mole degree	Solubility, g./100 cc.
Benzonitrile	27.86 ± 0.16	6.88 ± 0.46	2.9
Mixed benzonitrile (49.4% by weight) and veratrole	28.35 ± .16	8.06 ± .48	1.15
Decalin	29.37 ± .25	10.58 ± .71	0.19
Veratrole	30.04 ± .31	12.86 ± .90	9.24

Solvent Effects on the Activation Parameters.—In order to interpret the present solvent effects by means of the complexing theory, it is necessary to assume that some of the solvents solvate the transition state more and that others solvate the ground state more. For steric reasons, it seems likely that solvation of both types will be confined largely to the *p*-nitrophenylazo part of the molecule. There will be resonance contributions to the ground state corresponding to a negative charge on the oxygen of the nitro group and a positive charge on the benzene ring or adjacent azo group. This partial positive charge, or analogous structures in the solvent complex, will cause the ground state to be solvated by electron-rich molecules such as

veratrole. If such charged structures increase the strength of the bond being broken in the transition state, they will contribute less in the transition state than they do in the ground state. We may therefore expect veratrole to be released in the activation process with consequently higher enthalpy and more positive entropy for that solvent.

A similar argument suggests that the electron-poor ring of benzonitrile will complex more with the transition state and less with the ground state. We therefore expect a lowered enthalpy of activation and a less positive entropy for that solvent.

The mixture of benzonitrile and veratrole has a small molar excess of benzonitrile. The solubility data suggest that there is little or no free veratrole. We therefore expect the mixture to show activation parameters more like those for benzonitrile than like those for veratrole.

The Question of Radical versus Polar Reaction Mechanism.—It will be noted (Fig. 1) that the enthalpy of activation is approximately a linear function of the entropy of activation although the range is, unfortunately, not very large. A recent

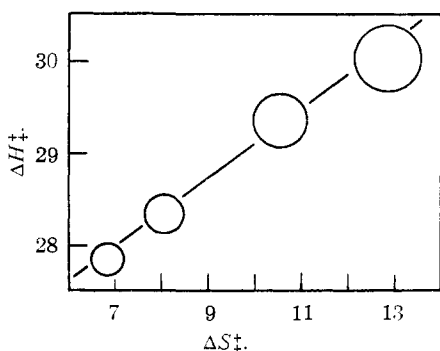


Fig. 1.

compilation by one of the authors⁶ shows that such relationships are very frequent and that when there are two mechanisms there are also two lines rather than one. It seems likely therefore that the reactions reported here are either all polar or all free radical in nature. Because the decomposition will initiate the polymerization of acrylonitrile in all solvents studied, we prefer the radical mechanism. The motive for the mixed benzonitrile-veratrole experiments was to encourage any polar reaction as much as possible by providing a solvent with components designed to stabilize each of two differently charged parts of a polar transition state. We have studied the products (but not the rate) of the reaction in absolute ethanol, a polar and nucleophilic solvent. Even in this solvent the products are the complex mixture to be expected of a radical reaction and the reaction still initiates the polymerization of acrylonitrile. Certain contrasts between the products from the substituted and unsubstituted azo compounds are pointed out in the Experimental section. We do not know whether they reflect a difference between the radicals or some degree of incursion by a polar side reaction. Neither the small-scale nitrogen evolution method nor the spectrophotometric method is satisfactory for

(6) J. E. Leffler, not yet published.

rate measurements of the substituted azo compound in ethanol.

Experimental

Tris-(*p*-anisyl)-methyl chloride was prepared by the method of Baeyer and Villiger,⁷ Lund,⁸ and Marvel.⁹

To a solution of 5.3 g. of the chloride in 500 cc. of dry ether was added a solution of 5.1 g. of *p*-nitrophenylhydrazine in a minimum of pyridine (about 10 cc.). The hydrochloride of *p*-nitrophenylhydrazine, which precipitated immediately, was removed by filtration and the solution concentrated by distillation including partial removal of the pyridine under vacuum. The residue solidified on trituration with methanol and then melted at 121.0–121.1°. Shaking the *p*-nitrophenylhydrazotris-(*p*-anisyl)-methane in benzene solution with excess silver oxide at room temperature for 36 hours converted it to the *azo* compound. The latter was induced to crystallize from the benzene solution after concentration to 15 cc. and addition of 45 cc. of methanol. Further purification was accomplished by adding methanol-water (3:1) to the dioxane solution until turbid, cooling to zero degrees, and collecting the crystals. The decomposition point varies with the rate of heating, the highest value observed being 130.8–131.1°; yield 4.6 g.

*Anal.*¹⁰ Calcd. for $C_{28}H_{28}N_3O_5$: C, 69.4; H, 5.56; N, 8.7. Found: C, 69.51; H, 5.58; N, 8.62, 8.65, 8.45.

Rate Measurements.—An optical method was abandoned when it was found that the products of the decomposition interfered. All the rates were measured by the pressure of nitrogen evolved at constant volume. The procedure used requires only a very small sample of azo compound. The magnetically stirred reaction flask and a control flask containing solvent are thermostated to $\pm 0.002^\circ$. Gas lines from the two flasks lead by way of concentric spirals in the same condenser jacket to a differential manometer containing diethyl phthalate. After pre-saturation with nitrogen (to reduce apparent induction period) the run is started by turning a ground joint which drops a small glass bucket of the azo compound into the reaction flask. It was our experience that this small scale method gives good results only with solvents of very low vapor pressure. Some of the runs were followed to completion to obtain an infinity value while others were calculated by the Guggenheim method.¹¹ In the several cases where both methods were used the agreement was satisfactory. First-order rate constants were calculated from at least fourteen and usually more than twenty points per run, using the method of least squares.

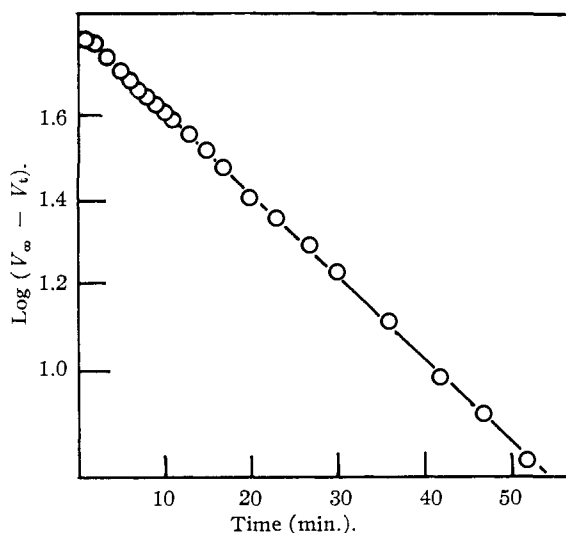


Fig. 2.—A typical decomposition in decalin.

- (7) A. Baeyer and V. Villiger, *Ber.*, **35**, 1189 (1902).
 (8) H. Lund, *THIS JOURNAL*, **49**, 1346 (1927).
 (9) C. S. Marvel, J. Whitson and H. W. Johnston, *ibid.*, **66**, 415 (1944).
 (10) Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.
 (11) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

Figure 2 shows a typical run. Some runs unusually aberrant from the activation enthalpy plot have been omitted, but this has not appreciably changed the values of the activation parameters or their probable errors.

Polymerization Experiments.—A solution of 0.0093 g. of *p*-nitrophenylazotris-(*p*-anisyl)-methane in 1 cc. of acrylonitrile and 5 cc. of decalin or anisole produced considerable turbidity at 50° in 24 hours. In 5 cc. of alcohol and 1 cc. of acrylonitrile, 0.015 g. of azo compound produced a considerable precipitate in four hours. In 5 cc. of pure acrylonitrile, 0.0093 g. of the azo compound produced complete solidification in 24 hours. All samples were sealed in glass tubes, cooled and evacuated to a pressure of 1 mm. or less.

The Products of the Reaction in Absolute Ethyl Alcohol.—An alcohol solution of *p*-nitrophenylazotris-(*p*-anisyl)-methane in a degassed and evacuated U-tube was allowed to decompose at 75°. The U-tube was cooled in liquid nitrogen, re-evacuated and the solvent completely distilled from one arm at room temperature, or slightly above, into the other arm at the temperature of liquid nitrogen. The distillate was found to contain nitrobenzene, identified by its ultraviolet absorption spectrum, in 46% of the theoretical

yield. The solid residue appeared to be a complicated mixture from which chromatography failed to isolate any pure substances. This is suggestive of a radical reaction. However, the solid residue was soluble in sulfuric acid and gave the characteristic spectrum of tris-(*p*-anisyl)-carbonium ion in the visible region with an intensity corresponding to a total yield of tris-(*p*-anisyl)-methyl oxygen and nitrogen compounds of 54% of the theoretical (see Fig. 3).

Comparison with the Decomposition Products of Phenylazotriphenylmethane in 95% Alcohol.—A similar experiment was carried out with the unsubstituted azo compound. It afforded benzene in 85% (or higher) yield, traces of triphenylmethane and traces of tetraphenylmethane all identified by their ultraviolet spectra and in the case of the latter two by melting points as well. The solid residue from the solvent stripping operation did not dissolve readily in concentrated sulfuric acid but gave a typical triphenylcarbonium ion spectrum in acetic acid-perchloric acid (25%). The yield of compounds capable of giving triphenylcarbonium ion was only 4% of the theoretical. Figure 4 shows the unknown and control spectra.

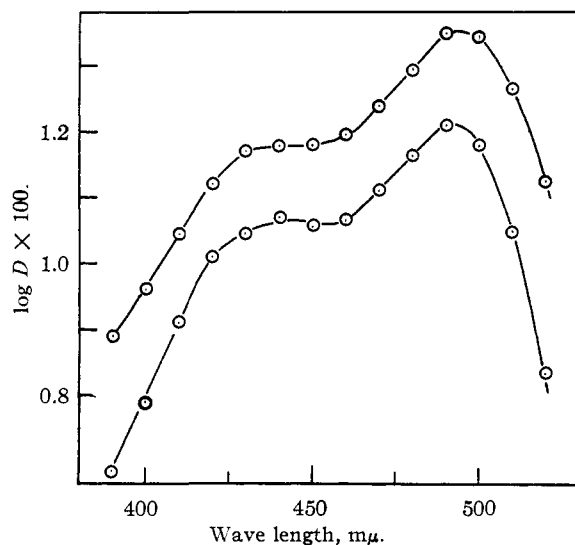


Fig. 3.—Upper curve: absorption in sulfuric acid by the non-volatile part of the products from the decomposition of *p*-nitrophenylazotris-(*p*-anisyl)-methane in alcohol. The concentration of the sulfuric acid solution corresponds to 2.22×10^{-5} mole of decomposed azo compound per liter. Lower curve: absorption in sulfuric acid by 6.33×10^{-6} molar tris-(*p*-anisyl)-methyl chloride.

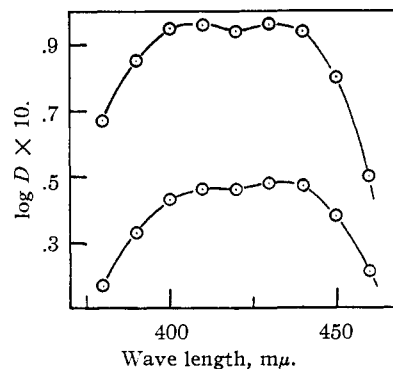


Fig. 4.—Upper curve: absorption by 3.16×10^{-5} molar triphenylmethyl ethyl ether in 75% acetic-25% perchloric acid. Lower curve: absorption in the same solvent by the non-volatile part of the products from the decomposition of phenylazotriphenylmethane in alcohol. The concentration of the acetic-perchloric acid solution corresponds to 2.84×10^{-4} mole of decomposed azo compound per liter.

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