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Studies of Sulfonyl Radicals. III.(1) Solvent Effects on the Thermal Decomposition of Benzyl Phenylazo Sulfone

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The first-order rate constants for thermal decomposition of benzyl phenylazo sulfone (BPA, **1**) have been determined spectrophotometrically in six solvents using the free radical scavenging technique with a stable Koelsch free radical. Activation parameters in the non-polar solvents such as benzene, toluene, anisole and chlorobenzene were almost the same, but in the two polar solvents, pyridine and nitrobenzene, activation entropies decreased significantly as compared with those in the non-polar solvents. This can be explained by the solvation of the polar solvent in the transition state leading to a phenyldiazenyl and α-toluenesulfonyl radical pair.

Although well established studies of solvent effects have been reported on many ionic reactions, definite information is still lacking as to free radical reactions, because of a weak interaction between free radical and solvent.

In connection with the studies on sulfonyl radicals(1,2a) and the propagation mechanism of free radical copolymerization of sulfur dioxide and styrene,(2b–d) we became interested in solvent effects on the thermal decomposition of benzyl phenylazo sulfone (BPA, $C_6H_5CH_2SO_2$–N=N–C_6H_5), since sulfonyl radicals ($RSO_2\cdot$) have a strong electrophilic character(1,3) and an unpaired electron is localized on the sulfonyl groups.(1) Sulfonyl radicals are thus expected to behave as an electron acceptor(4) and to interact with polar or electron donating solvents. Activation parameters for the decomposition of *p*-tolyl phenylazo sulfone (TPA), which forms(6) *p*-toluenesulfonyl and phenyl radicals, are found(5) to change with solvents remarkably; in ethylbenzene $\Delta H^{\ddagger}=30.8$ kcal/mol, $\Delta S^{\ddagger}=10.7$ e.u. and in *N,N*-dimethylformamide $\Delta H^{\ddagger}=39.6$ kcal/mol, $\Delta S^{\ddagger}=34.4$ e.u. This is in striking contrast to the results reported on the thermal decomposition of 2,2′-azobisisobutyronitrile, *i.e.*, the maximum difference among the activation parameters determined in several solvents is found to be $\Delta\Delta H^{\ddagger}=1.78$ kcal/mol and $\Delta\Delta S^{\ddagger}=4.96$ e.u.(7)

We have determined the rate constants for BPA decomposition by using the radical scavenging technique with a stable radical, α,γ-bisdiphenylene-β-phenylallyl (Koelsch radical). The existence of radical-induced decomposition sometimes makes it difficult to determine a rate constant of unimolecular decomposition.(8) The unimolecular rate constsnt in BPA thermal decomposition, however, can be exclusively determined by the use of Koelsch radical (by capturing the radicals formed in the decomposition).(9)

Experimental

Materials. Benzyl phenylazo sulfone (BPA) was prepared by the reaction of benzene diazonium salt with sodium α-toluenesulfinate prepared(10) by treatment of α-toluenesulfonyl chloride with sodium sulfite and sodium hydrogencarbonate in water. Crude BPA was recrystallized several times from ethanol: mp 90—92 °C (dec) (lit,(9) 97—99 °C). (Found: C, 60.27; H, 4.60; N, 11.16%. Calcd for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76%.). The Koelsch radical was prepared according to the method of Kuhn and Neugebauer,(11) and recrystallized several times from benzene. Since Koelsch radical is known to crystallize from benzene in a 1 : 1 ratio with the solvent, the benzenated radical was pumped at 100 °C to constant weight (70 h). Found: C, 94.19; H, 5.06%. Calcd for $C_{33}H_{21}$: C, 94.93; H, 5.07%.). Galvinoxyl was prepared from 2,6-di-*t*-butylphenol.(12) Purity of this compound was given as 97.3% by a comparison of molar extinction coefficient with the reference value.(12) All the solvents were purified by distillation in the presence of Koelsch radical or DPPH just before use.

General Procedure. The rate at which BPA decomposes to give radicals scavenged by Koelsch radical was measured in the UV cell (1 cm path length). The cell, containing BPA, Koelsch radical and the solvent, was connected to a vacuum system through a stopcock, the solution being degassed by freeze-pump-thaw cycles. After the fourth freeze-pump-thaw cycle, the system was closed and disconnected from the vacuum system. The absorbance was then measured at 780 nm for Koelsch radical (shoulder) and at 769 nm for galvinoxyl (absorption maximum). The cell set in a Cary 14 UV spectrophotometer was thermostated at a definite temperature by the circulation of thermostated water into the cell holder. The temperature of the solution in the cell was determined by measuring the temperature of an identical solvent in another cell with a copper-constantan thermocouple.

Results and Discussion

Rate Constants for the Unimolecular Thermal Decomposition of BPA. The rate constants obtained by varying the concentration of BPA at 60 °C (Table 1) are considered to be of the real first-order, since each rate constant is not dependent upon the concentration of BPA. If Koelsch radical is highly effective in capturing all the radicals produced and if BPA is in large excess, a plot of time *vs.* absorbance of the Koelsch radical should follow zero-order kinetics with respect to the disappearance of Koelsch radical. A typical plot for the benzene solution is shown in Fig. 1. It follows that the first-order rate constants for the BPA decomposition can be calculated by

$$2k[\mathrm{BPA}]_0=k_0 \qquad (1)$$

where k_0 and k are the zero-order rate constant (slope of Fig. 1) for the disappearance of Koelsch radical and the first-order rate constant for the thermal decomposition of BPA (it should be noted that the first-order rate constants obtained here include the efficiency of diffusion from solvent cage).

In the case of nitrobenzene, however, a plot of time *vs.* absorbance did not give a straight line; the rate of

Table 1. First-order rate constants obtained with Koelsch radical for thermal decomposition of benzyl phenylazo sulfone in solutions at 60 °C

Solvent	$[BPA]_0\times10^3$ (mol/l)	$k\times10^6$ (s^{-1})	$k_{av}\times10^6$ (s^{-1})
Benzene	5.85	19.1	
	5.86	18.5	
	11.7	18.4	
	11.7	16.4	17.9
Benzene[a)]	5.96	19.5	
	11.7	21.0	
	23.7	18.4	19.6
Toluene	11.8	18.4	
	11.9	17.7	
	24.6	17.6	17.9
Anisole	11.8	10.3	
	17.9	11.0	
	17.9	10.3	
	23.3	9.8	
	23.8	10.8	10.4
Chlorobenzene	12.9	11.3	
	19.3	11.5	11.4
Pyridine	23.6	12.1	
	35.3	13.1	12.6
Nitrobenzene[b)]	26.6	3.13	
	32.2	3.28	
	45.6	2.62	3.01

a) Galvinoxyl used as stable free radical. b) Values obtained by extrapolating to zero concentration of Koelsch radical.

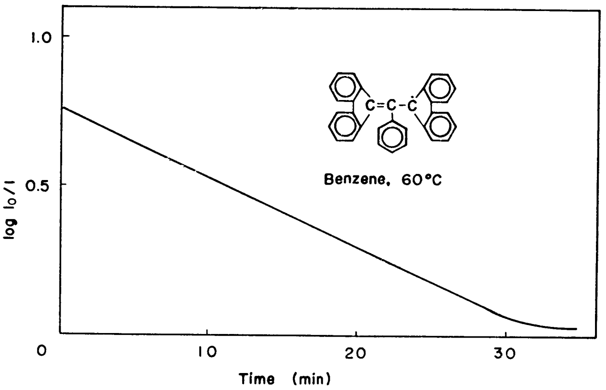
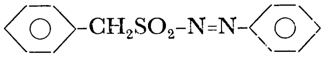


Fig. 1. Plot of absorbance at 785 nm *vs.* time for the thermal decomposition of BPA (5.83×10^{-3} mol/l) in the presence of the Koelsch radical (9.40×10^{-4} mol/l) in benzene at 60 °C.

the disappearance of Koelsch radical diminished with decreasing concentration, suggesting the occurrence of an induced decomposition by Koelsch radical in nitrobenzene. Thus, the first-order rate constant in this solvent was determined by extrapolation of the disappearance rates to zero concentration of Koelsch radical.

For BPA decomposition in benzene galvinoxyl has also been used as a stable radical (Table 1). Almost the same values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as those in the case of Koelsch radical are obtained (Table 2), supporting the above conclusion, *viz.*, the values obtained are the real first-order rate constants. The rate constant in benzene solution using Koelsch radical ($1.79\times10^{-5}\,s^{-1}$ at 60 °C) is approximately the same as the value reported by Kice and Gabrielsen ($1.3\times10^{-5}\,s^{-1}$ at 60 °C).[9)]

Strong Solvation of Polar Solvents in the Transition State. The rate constants obtained at 45—70 °C and the activation parameters in six solvents are shown in Table 2. The activation parameters in four non-polar solvents, benzene, toluene, anisole, and chlorobenzene, are almost the same within experimental error, but those obtained in two polar solvents, pyridine and nitrobenzene, decrease as compared with the values in non-polar solvents, indicating a strong solvation of pyridine or nitrobenzene in the transition state. Since BPA decomposition reaction is endothermic (Table 2), the transition state resembles products (in this case the sulfonyl and the diazenyl radicals) more than starting material, according to Hammond postulate. The contribution of the charge transferred resonance form shown below would be a possible explanation for the polar character of the transition state, in which the polar solvents solvate.



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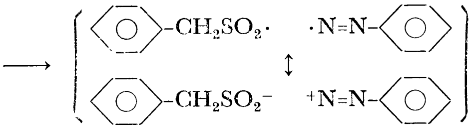

The radical pair may be stabilized by the contribution of the charge transfer between α-toluenesulfonyl radical and phenyldiazenyl radical due to the strong electron accepting nature of the former. In the thermal decomposition of alkyl arylazo sulfide (alkyl–S–N=N–Ar) the significant changes in activation parameters with solvents have been explained by the formation of ion-pair, alkyl–S⁻ ⁺N=N–Ar.[13)]

The isokinetic relation was plotted to give a straight line with an isokinetic temperature of 30 °C (Fig. 2, $\Delta H^{\neq}$ (34.1±2.1 kcal/mol) and $\Delta S^{\neq}$ (21.7±6.3 e.u.), obtained in the cyclohexane-benzene mixed solvent (5 : 1, vol. ratio), were also plotted).

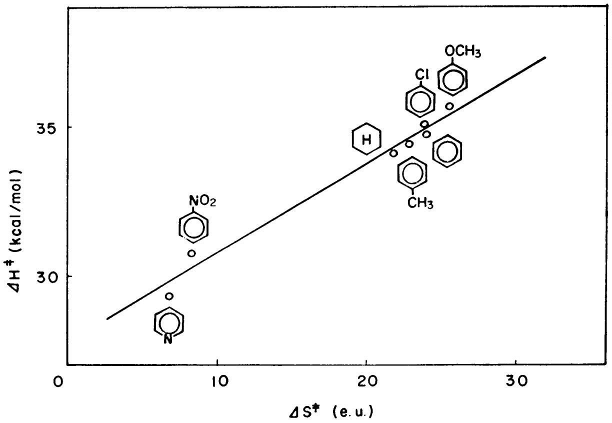

Fig. 2. Plot of isokinetic relation.

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS OBTAINED WITH KOELSCH RADICAL FOR THERMAL DECOMPOSITION OF BENZYL PHENYLAZO SULFONE IN SOLUTIONS

Solvent	Runs[a]	Temp (°C)	$k_{av} \times 10^6$ (s^{-1})	$\Delta H^{\ddagger}$[b] (kcal/mol)	$\Delta S^{\ddagger}$[b] (e. u.)
Benzene	3	70.2	88.3		
	3	65.0	40.9		
	4	60.0	17.9		
	9	55.0	8.05	34.8±0.8[c]	23.9±2.3[c]
Benzene[d]	2	65.0	42.4		
	3	60.0	19.6		
	3	55.0	8.60		
	2	49.8	3.43	35.4±1.1	25.8±3.2
Toluene	3	65.0	39.5		
	3	60.0	17.9		
	3	55.0	8.13		
	3	50.0	3.47	34.4±0.1	22.7±0.4
Anisole	3	70.0	51.3		
	5	65.0	23.4		
	5	60.0	10.4		
	2	55.0	4.48	35.7±0.4	25.6±1.3
Chlorobenzene	2	70.0	55.7		
	2	65.0	25.9		
	2	60.0	11.4		
	2	55.0	5.14	35.0±0.3	23.8±1.0
Pyridine	2	60.0	12.6		
	3	55.0	6.22		
	3	50.0	2.96		
	3	45.0	1.51	29.3±1.2	6.8±3.6
Nitrobenzene	3	70.0	12.9		
	3	65.0	6.21		
	3	60.0	3.01		
	3	55.0	1.59	30.7±1.8	8.2±5.4

a) Measurements carried out with varying concentration of BPA. b) By the least-square method. c) Standard deviation. d) Galvinoxyl used as stable free radical.

The rate constants obtained here include the efficiency in cage effect (f). A preliminary experiment gave $f=$ 0.56 for the benzene solution at 80 °C. It seems that the change in f with the solvents gives little effect on the activation parameters.

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