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Decomposition of Benzenediazonium Tetrafluoroborate in Aprotic Polar Solvents

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The decomposition of aryldiazonium tetrafluoroborate has been investigated in dimethyl sulfoxide, acetonitrile, nitromethane, dimethylformamide and acetone.

Experimental

Materials. Dimethyl sulfoxide was dried with calcium hydride and distilled at 86°C/25 mmHg. Acetonitrile was refluxed with phosphorus pentoxide, and then distilled at 81°C. Nitromethane was dried with calcium chloride and then distilled at 101°C. Dimethylformamide was distilled at 153°C. Acetone was treated according to the method of Hudson and Wardill,1) and distilled at 56.5°C. Benzenediazonium tetrafluoroborate was prepared by the addition of an aqueous hydrogen tetrafluoroborate solution to a benzenediazonium chloride solution obtained from the aniline purified by distillation at 109°C/30 mmHg. The crystals were filtered, washed successively with cold water, ethanol and ether, and then they were dried *in vacuo*.

Kinetic Measurements. The diazonium salt was decomposed in a water bath, the temperature of which was regulated within ±0.1°C. The rate of decomposition was followed by measuring the evolution of nitrogen gas by use of a gas burette.

Results and Discussion

The decomposition of benzenediazonium tetrafluoroborate in these solvents were of first order. The first-order rate constants in these five solvents are shown in Table 1. Figure 1 shows the plots of $\log k$ *versus* $1/T$, and the activation parameters obtained from Fig. 1 are shown in Table 2. Figure 2 shows that the values of activation energies and activation entropies fit an isokinetic relationship very well. The activation entropy was small in a solvent with a small activation energy, and *vice versa*. The isokinetic temperature was 311°K.

It was found that the decomposition of benzenediazonium tetrafluoroborate in DMSO yielded

TABLE 1. FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF PhN_2BF_4

in DMSO		in CH_3CN		in DMF		in CH_3NO_2		in $(CH_3)_2CO$	
Temp. (°C)	$k_1\times10^4$ (sec^{-1})	Temp. (°C)	$k_1\times10^4$ (sec^{-1})	Temp. (°C)	$k_1\times10^4$ (sec^{-1})	Temp. (°C)	$k_1\times10^4$ (sec^{-1})	Temp. (°C)	$k_1\times10^4$ (sec^{-1})
24.0	0.388	30.2	0.685	30.2	0.778	25.1	0.294	35.0	1.34
30.0	1.000	35.0	1.68	35.0	1.792	30.1	0.711	39.8	2.87
34.0	1.82	39.8	2.84	39.8	3.17	35.5	1.87	44.3	4.84
40.3	3.84	44.8	6.91	44.8	9.27	40.1	4.39		
45.7	8.61								

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1) R. F. Hudson and J. E. Wardill, *J. Chem. Soc.*, **1950**, 1731.

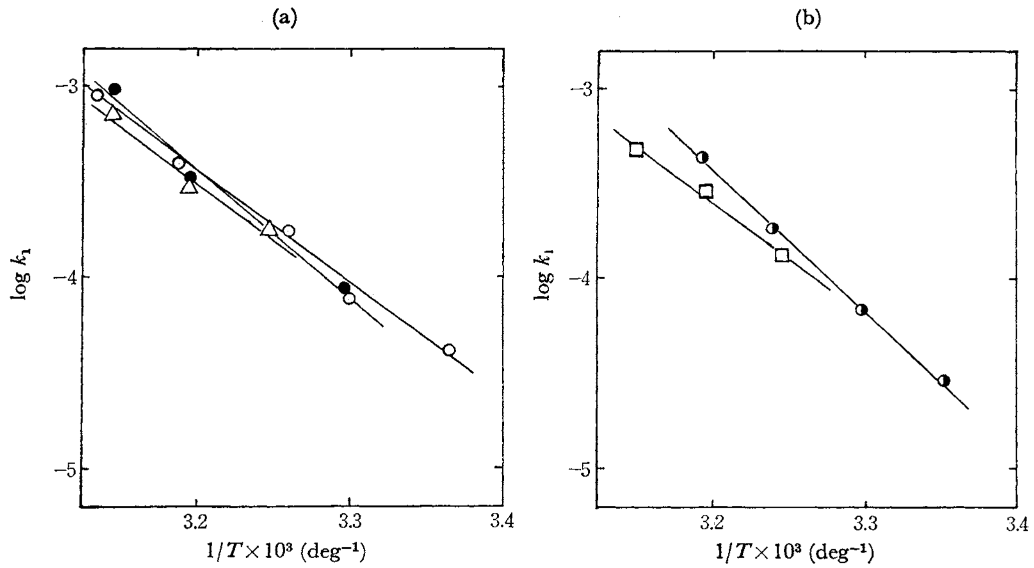

Fig. 1. Arrhenius plots for the decomposition of PhN_2BF_4.
○: in DMSO, △: in CH_3CN, ●: in DMF,
◑: in CH_3NO_2, □: in $(CH_3)_2CO$

Table 2. Activation parameters for the decomposition of PhN_2BF_4

Solvent	E_a (kcal/mol)	$\Delta S^{\ne}_{25^\circ C}$ (e.u.)
$(CH_3)_2CO$	26.9	9.2
DMSO	27.1	10.4
CH_3CN	29.7	18.3
DMF	31.6	24.7
CH_3NO_2	33.5	30.9

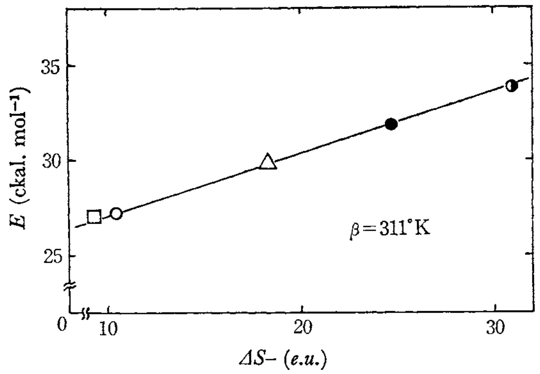

Fig. 2. Isokinetic relationship for the decomposition of PhN_2BF_4.
□: in $(CH_3)_2CO$, ○: in DMSO, △: in CH_3CN,
●: in DMF, ◑: in CH_3NO_2

7.8% of 1,3-benzoxathian, 25.0% of phenol and 32.5% of *o*-hydroxybenzyl methyl sulfide. The results of both kinetic studies and product studies are best explained by the monomolecular decomposition of the diazonium ion to phenyl cation and nitrogen.

Thus, the decomposition in these aprotic polar solvents is in quite a contrast with the decomposition in methanol[2] or in pyridine,[3] in which the decomposition was homolytic and phenyl radical was the intermediate. Methanol and pyridine are rather strong nucleophiles, and attack the diazonium cation to yield a diazoether or a triazene, which undergoes homolyses. The nucleophilicity of the solvents used in this investigation was not strong enough to cause the combination with the diazonium ion. However, the polarity of these solvents is apparently large enough to assist the formation of phenyl cation stabilized by solvation.

It was found that the rate of decomposition of benzenediazonium tetrafluoroborate in an aqueous DMSO solution was approximately the same as that in pure DMSO. This indicates that the mechanism of decomposition in an aprotic polar solvent is similar to the mechanism reported for decomposition in water.[4a,4b]

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[2] D. F. DeTar and M. N. Turetzky, *J. Amer. Chem. Soc.*, **77**, 1945 (1955); **78**, 3925 (1956).

[3] R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).

[4] a) M. L. Crossley, R. H. Kiene and C. H. Benbrook, *J. Amer. Chem. Soc.*, **62**, 1400 (1940); E. S. Lewis and E. B. Miller, *ibid.*, **75**, 429 (1953); D. F. DeTar and A. R. Ballentine, *ibid.*, **78**, 3916 (1956); D. Schule-Frohlindo and H. Blume, *Z. Phys. Chem. Neue Folge*, **59**, 299 (1968).