February, 1980] © The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 53, 551—552 (1980) 551

Complexation of Arenediazonium Ions with a Macrocyclic Polyether. The Stability Constants for the Complexes

Yoji HASHIDA* and Kohji MATSUI
Department of Synthetic Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

(Received May 10, 1979)

Synopsis. The stability constants for 18-crown-6 complexes with arenediazonium salts have been determined spectrophotometrically. The Hammett plot for *m*- and *p*-substituted benzenediazonium salts showed good correlation with a reaction constant 0.98 in methanol. The solvent effect on the stability of the complexes has been discussed.

Complexation of arenediazonium ions with macrocyclic polyethers, *i.e.* crown ethers, have been elucidated by NMR[1,2] and IR[3] spectroscopy. Such complexation with the appropriate crown ether reduces the thermal[4] and photochemical[5] decomposition of arenediazonium ions. Several preparative uses for crown ethers which include halogen displacement[6] and effective arylation[7,8] of aromatic substrates have been explored. This note will deal with the stability constants (K_S) for the 18-crown-6 complexes with arenediazonium salts:

$$\text{Ar-N}_2{}^+\text{BF}_4{}^- + \text{P} \overset{K_s}{\rightleftarrows} \text{Ar-N}_2{}^+,\ \text{P},\ \text{BF}_4{}^- \qquad (1)$$

$$K_s = [\text{Ar-N}_2{}^+,\ \text{P},\ \text{BF}_4{}^-]/[\text{Ar-N}_2{}^+\text{BF}_4{}^-][\text{P}]$$

where P denotes the crown ether. 18-Crown-6 was chosen as the host, since it has an appropriate cavity size for the diazonium ion,[2] and is transparent in the UV region.

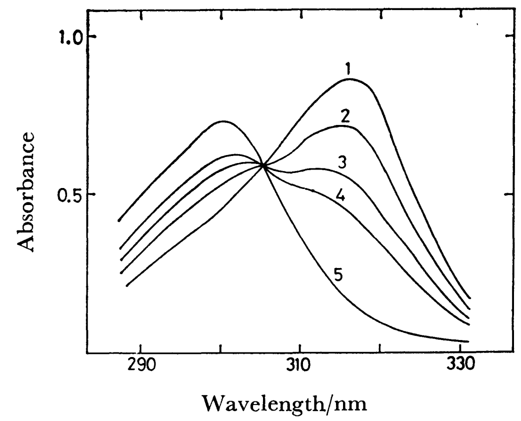

Fig. 1. UV spectrum of *p*-methoxybenzenediazonium tetrafluoroborate in chloroform in the absence and presence of 18-crown-6; $[\text{Ar-N}_2{}^+\text{BF}_4{}^-]_0 = 2.19\times10^{-5}$ M, (1), $[\text{P}]_0=0$, (2) $[\text{P}]_0=1.2\times10^{-4}$ M, (3), $[\text{P}]_0=2.3\times10^{-4}$ M, (4) $[\text{P}]_0=4.7\times10^{-4}$ M, (5) $[\text{P}]_0=5.2\times10^{-2}$ M (Further addition of the crown ether did not change the spectrum).

It has been found that the absorption maxima of arenediazonium ions shift to shorter wavelengths on complexation with the crown ether. Figure 1 shows a typical spectral change for the *p*-methoxybenzenediazonium salt in chloroform with increasing addition of 18-crown-6. The difference in UV spectra was used as an analytical tool to determine the stability constant, by adding known amounts of diazonium salt and crown compound into the solvent (see Experimental).

The stability constants measured in several organic solvents are given in Table 1, together with the spectral properties of diazonium ions and their complexes. The

TABLE 1. STABILITY CONSTANTS (K_S) FOR THE 18-CROWN-6 COMPLEXES WITH (X)-SUBSTITUTED BENZENEDIAZONIUM TETRAFLUOROBORATES AT 15 °C

No.	Substituent (X)	Solvent	ε[a]	E_T[b]	pK_a[c]	$\log K_s$[d]	λ^{Dz}_{max}/nm[e]	λ^{Cx}_{max}/nm[e]
1	p-NO_2	Methanol	32.7	55.5	−2.2	3.10	256	249
2	p-CN	Methanol				3.15	262	255
3	m-Cl	Methanol				2.71	261	251
4	m-OCH_3	Methanol				2.63	275	260
5	H	Methanol				2.46(2.37)[f]	259	247
6	p-CH_3	Methanol				2.39(2.26)[f]	275	266
7	p-OCH_3	Methanol				2.09	311	297
8	p-$N(CH_3)_2$	Methanol				1.56	380	362
9	p-OCH_3	Dioxane	2.2	36.0	−2.92	1.87	309	302
10	p-OCH_3	THF	7.6	37.4	−2.08	2.27	309	299
11	p-OCH_3	Acetone	20.7	42.2	−7.2	2.56	327	323
12	p-OCH_3	CH_2Cl_2	9.1	41.1		3.23	328	295
13	p-OCH_3	$CHCl_3$	4.8	39.1		3.45	317	301
14	p-OCH_3	$ClCH_2CH_2Cl$	10.4	41.9		4.67	321	298
15	p-CH_3	$ClCH_2CH_2Cl$				5.10	282	264
16	o-CH_3	$ClCH_2CH_2Cl$				3.97	270	250
17	2,6-$(CH_3)_2$	$ClCH_2CH_2Cl$				2.01	274	265

a) Dielectric constant of solvent (from Ref. 16). b) Ref. 13. c) Ionization constant of conjugate acid of solvent (from Ref. 16). d) K_s: M^{-1} e) Maximum wavelength for the free diazonium ion (λ^{Dz}_{max}) and its complex (λ^{Cx}_{max}). f) Ref. 9.

observed stability constants are in reasonable agreement with those determined by titration calorimetry (Nos. 5, 6).[9]

One interesting aspect in Table 1 is the structural effect of diazonium salts on the stability of the complexes. The stability constant depended on the nature of the substituent in the diazonium salt as expected, *i.e.* as the electrophilicity of the diazonio group increases, the stability of the complex increased. The Hammett plot for the *m*- and *p*-substituted compounds (Nos. 1—8) shows a good correlation; a least-squares treatment gives an equation, $\log K_S = 0.98\sigma + 2.43$ with a correlation coefficient (r) of 0.986. The ρ value found is relatively low compared with those in other diazo-equilibrium systems, such as arenediazocyanide-($\rho=3.53$),[10] arenediazosulfone-($\rho=3.76$),[11] arenediazosulfonate)-($\rho=5.5$),[12] and arenediazotate-formation ($\rho=6.58$).[10] Ortho-substitution on the diazonium ion considerably reduces complex stability; the introduction of the *o*-methyl (No. 16) and 2,6-dimethyl groups (No. 17) lowered the $\mathrm{p}K_S$ by *ca.* one and three units respectively. This behavior undoubtedly results from steric hindrance.[2]

It was shown that the solvent has a pronounced effect on the stability (Nos. 7, 9—14). As can be seen, there is no observable correlation between stability of the complex and the common solvent properties such as dielectric constant and E_T-value.[13] Rather, the stability of the complex appears to be influenced by the basicity of the solvent, *i.e.* relatively stable complexes were formed in less basic solvents such as acetone and chlorinated alkanes.[14] This is explainable since the free diazonium ion is more stabilized by significant solvation in a solvent of higher basicity.

Experimental

Materials. 18-Crown-6 was prepared as described in the literature[15] (mp 38—40 °C). Arenediazomiun fluoroborates were prepared using reagent grade aromatic amines and purified by dissolving them in the minimum amount of acetonitrile, followed by reprecipitation with the addition of diethyl ether. The solvents were purified by standard procedures.[16]

$\mathrm{p}K_S$ Measurement. A solution of the diazonium salt *ca.* 2×10^{-4} M ($1\ \mathrm{M}=1\ \mathrm{mol\ dm^{-3}}$) was prepared. In a typical run, a sample (5 ml) of this solution was added to a mixture of MeOH–H_2O (1 : 1, in volume) containing the R-salt (2-naphthol-3,6-disulfonic acid) and sodium carbonate; the solution was subsequently diluted to a specified volume and the absorbance measured, in order to determine the original concentration of diazonium salt. The remaining diazonium solution was employed for $\mathrm{p}K_S$ measurements; known quantities of the solution were added to a solution containing specified amounts of crown ether and the optical spectrum recorded at 15 °C. The stability constant K_S based on the Eq. 1 was calculated using a spectrally determined $[\mathrm{Ar{-}N_2^+, P, BF_4^-}]/[\mathrm{Ar{-}N_2^+BF_4^-}]$ ratio under a given condition, in conjuction with the following equations;

$$[\mathrm{Ar{-}N_2^+BF_4^-}]_0 = [\mathrm{Ar{-}N_2^+BF_4^-}] + [\mathrm{Ar{-}N_2^+, P, BF_4^-}]$$

$$[\mathrm{P}]_0 = [\mathrm{P}] + [\mathrm{Ar{-}N_2^+, P, BF_4^-}]$$

where $[\mathrm{Ar{-}N_2^+BF_4^-}]_0$ and $[\mathrm{P}]_0$ denote the original concentrations of diazonium salt and the crown ether, respectively.

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