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Influence of Steric and Electronic Effects on the Binding of Arenediazonium Cations to 18-Crown-6 in Methanol at 25 °C[1a]

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Abstract: Log K, ΔH, and $T\Delta S$ values for the interaction of several arenediazonium salts with 18-crown-6 were determined in methanol at 25 °C by the calorimetric titration technique. The complex of benzenediazonium cation with 18-crown-6 is enthalpy stabilized with log $K = 2.50$. Substitution of a methyl group onto the ortho position(s) of benzenediazonium cation results in a total loss of complex stability. Substitution of various groups onto the para position results in changes in complex stability according to the electronic effect exerted in the diazonium moiety. A linear Hammett relationship ($\rho = 0.65$) was found between log K and σ_p^+ values associated with the para substituent.

Introduction

Macrocyclic ligands are known to bind many metal cations by sequestering them within the macrocyclic ligand cavity.[2] In similar fashion, 18-crown-6 was shown first by Gokel and Cram[3] and subsequently by Haymore et al.[4] and by Kyba et al.[5] to complex benzenediazonium cation ($PhNN^+$) in solution with the insertion of the diazonium moiety into the ligand cavity. The formation of such complexes has been exploited by Bartsch and his co-workers[6] to enhance the stability of arenediazonium cations against decomposition. These workers found that the rate of thermal decomposition of p-t-$BuC_6H_4NN^+$ ion in organic solvents and of photochemical decomposition of diazonium ions in the solid phase are significantly reduced by addition of crown ethers. The ligand 18-crown-6 (18C6) was more effective in stabilizing these cations than 15-crown-5.

We reported in a previous communication[7] that the value of the stability constant of the 18C6 complex of benzenediazonium cation is very sensitive to steric interference from substituent groups in the ortho positions as was demonstrated qualitatively by Gokel and Cram[3] and by Kyba et al.[5] We here report the details of this study and the effect on complex stability of substituents in the para position which exert varying electronic influence on the diazonium moiety.

Experimental Section

Materials. The 18C6 (Parish Chemical) was used without further

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Table I. Log K, ΔH, and $T\Delta S$ Values for Reaction in Methanol at 25 °C of Arenediazonium and Anilinium[a] Cations with 18-Crown-6

cation[b]	log K	ΔH[c]	$T\Delta S$[c]
$PhNH_3^+$	3.80	−9.54	−4.4
$2\text{-}CH_3C_6H_4NH_3^+$	2.86	−7.59	−3.7
$2,6\text{-}(CH_3)_2C_6H_3NH_3^+$	2.00	−5.65	−2.9
$PhNN^+$	2.50	−8.41	−5.0
$2\text{-}CH_3C_6H_4NN^+$		[d]	
$2,6\text{-}(CH_3)_2C_6H_3NN^+$		[e]	

[a] From ref 10. [b] Anion is BF_4^- (arenediazonium salts) or Br^- (anilinium salts). [c] kcal/mol. [d] No measurable heat.[12] [e] Cation decomposes too rapidly to allow accurate measurement.

purification. The methanol used (Fisher reagent) was found to contain less than 0.04% water by Karl Fischer titration.

Diazonium salts were prepared by the usual method[8] from substituted anilines, $NaNO_2$, and HCl at 0 °C. The BF_4^- salts were crystallized from solution by the addition of 48% HBF_4. The crude crystalline solids were recrystallized several times from methanol-ether and dried by placing them under vacuum for a short time. The resulting diazonium salts were 94–99% pure and contained no reactive impurities. The salts were stored as solids at −20 °C and methanol solutions for calorimetric titration were prepared immediately prior to use. Except for $2,6\text{-}(CH_3)_2C_6H_3NN^+BF_4^-$, the diazonium salts showed no observable decomposition in solution during the thermometric titration. The decomposition of $2,6\text{-}(CH_3)_2C_6H_3NN^+BF_4^-$ in solution was sufficiently slow that the absence of any heat of complexation could be determined.

Procedure. The calorimetric titration procedure for determining log K, ΔH, and $T\Delta S$ for the reaction between ligand and cation has been described.[9] A 0.15 M methanolic solution of 18C6, used as titrant, was standardized by calorimetric titration to an end point against a standard methanol solution of anhydrous KBr. Solutions of the diazonium salts in methanol (0.007 M) were used as the titrate. Because the heat produced in the reaction with $p\text{-}N(CH_3)_2C_6H_4NN^+BF_4^-$ was small, more concentrated solutions were used: 0.5 M titrant and 0.01 M titrate. A computer program (EQDHAD) allowed the concentration of cation to be varied during the calculation of log K and ΔH so that the purity of the cation could be determined.

Results and Discussion

The thermodynamic data from this study show that stabilities of complexes between 18C6 and various arenediazonium ions are strongly dependent on both steric and electronic effects.

Steric Effects. X-ray crystallography has shown that the mode of binding of (a) $PhNN^+$ cation[10] and (b) $PhNH_3^+$ cation[11] to 18C6 corresponds to the simplified structures in Figures 1a and 1b, respectively. These structures imply that the aromatic group of the diazonium ion is drawn much closer to the cyclic polyether ligand than the aromatic group of the anilinium ion. For this reason, substitution of bulky groups on the ortho positions of $PhNN^+$ is expected to interfere more severely with the complexation process than analogous substitution on $PhNH_3^+$.

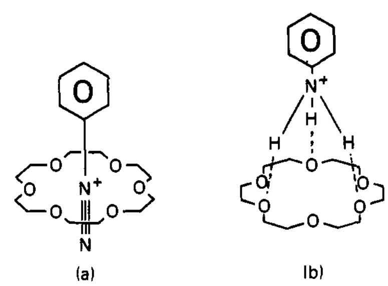


Figure 1. Diagrammatic representation of mode of binding of (a) benzenediazonium ($PhNN^+$) and (b) anilinium ($PhNH_3^+$) cations to 18-crown-6 (18C6). Dashed lines represent hydrogen bonds.

In Table I are listed log K, ΔH, and $T\Delta S$ values for the interaction of $PhNN^+$, and two of its ortho-substituted analogues with 18C6 in methanol at 25 °C together with corresponding data for $PhNH_3^+$ and its analogues which were reported earlier[12] and are presented here for comparison purposes. Both $PhNN^+$ and $PhNH_3^+$ form strongly enthalpy-stabilized complexes with this ligand, although the stability constant for the $PhNH_3^+$ complex is an order of magnitude larger. Substitution of one methyl group onto one ortho position of $PhNH_3^+$ causes the stability constant to drop in value by almost an order of magnitude. By contrast, similar substitution onto $PhNN^+$ results in a total loss of enthalpic stabilization and complex stability.[13] Substitution of an additional methyl group to give $2,6\text{-}(CH_3)_2C_6H_3NH_3^+$ results in further loss of complex stability, while the corresponding $2,6\text{-}(CH_3)_2C_6H_3NN^+$ cation does not react with 18C6. These results are consistent with those predicted from steric considerations as described above. Substitution onto the ortho positions has a greater destabilizing effect on the diazonium than on the anilinium complexes.

The rather regular stepwise loss of complex stability through the series $C_6H_5NH_3^+$, $2\text{-}CH_3C_6H_4NH_3^+$, $2,6\text{-}(CH_3)_2C_6H_3NH_3^+$ is a result of less favorable enthalpy changes. Indeed, the corresponding entropy changes favor greater complex stability through this series. Because the $PhNN^+$ complex is also enthalpy stabilized, the loss of stability upon ortho substitution is probably also caused by less favorable enthalpy changes.

Electronic Effects. Substitution at the para position of $PhNN^+$ results in variation of the stabilities of complexes formed with 18C6, even though steric hindrance at the coordination site is not significant. Rather, the degree to which complex stability is affected correlates with the electronic

Table II. Log K, ΔH, and $T\Delta S$ Values[a] for Reactions of $p\text{-}RC_6H_4NN^+$ with 18-Crown-6 (Methanol, 25 °C)

R	σ[b]	σ_p^+	log K	ΔH[c]	$T\Delta S$[c]	diazonium salt purity, %
NO_2	0.78	0.79	3.02 ± 0.02	−8.39 ± 0.07	−4.3	96 ± 1
CF_3	0.52	0.52	2.85 ± 0.02	−8.90 ± 0.09	−5.0	98 ± 1
Cl	0.14	0.11	2.62 ± 0.03	−8.65 ± 0.07	−5.1	94 ± 2
H[d]	0.00	0.00	2.50 ± 0.08	−8.4 ± 0.2	−5.0	96 ± 2
F	0.00	−0.07	2.52 ± 0.03	−8.57 ± 0.11	−5.1	99 ± 1
CH_3[d]	−0.26	−0.31	2.30 ± 0.01	−8.6 ± 0.3	−5.5	99 ± 1
OCH_3	−0.63	−0.78	2.01 ± 0.02	−8.1 ± 0.2	−5.4	96 ± 3
$N(CH_3)_2$	−1.44	−1.70	0.9 ± 0.1[e]	−6.5 ± 0.7[e]	−5[e]	100[e]
			0.9 ± 0.1[e]	−6.9 ± 0.6[e]	−6[e]	95[e]

[a] Reported as average of three or more independent determinations and standard deviation from the mean. [b] $\sigma = \sigma_I + 0.88\sigma_R^+$ [c] kcal/mol. [d] These data supplant those reported previously.[7] [e] Because log K is so small, these data did not permit accurate determination of diazonium salt purity as described in the Experimental Section. Therefore, a range of values is given for log K, ΔH, and $T\Delta S$ within which the true values are expected to lie, assuming that the diazonium salt is between 100 and 95% pure.

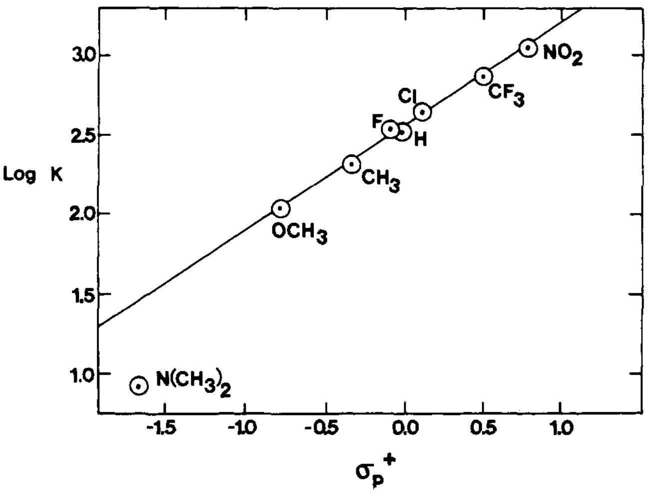
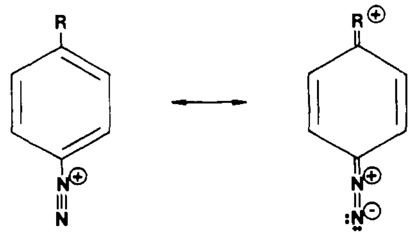


Figure 2. Plot of log K for formation in methanol at 25 °C of the 18C6 complex of p-$RC_6H_4NN^+$ vs. Hammett $\sigma_p{}^+$ values of R.

resonance and induction effects of the para substituent on the diazonium ion. The log K, ΔH, and $T\Delta S$ values for reaction of various para-substituted $PhNN^+$ cations are given in Table II along with the corresponding values[14] of $\sigma_p{}^+$. Use of the parameter $\sigma_p{}^+$ takes into account the ability of the diazonium moiety to withdraw electrons from the ring according to the following resonance structures.



The data in Table II show that, as the para substituent becomes more electron donating, the complex formed with 18C6 decreases in stability. Indeed, complex stability is almost completely lost when the para substituent is $N(CH_3)_2$ or $N(C_2H_7)_2$.[7] Thus, the cations with the more effective positive charge on the nitrogen atoms of the diazonium ion form the stronger complexes.

Figure 2 shows that a straight-line relationship exists between the values of $\sigma_p{}^+$ and log K for the interaction of 18-crown-6 with p-$RC_6H_4NN^+$. Only the data for p-$N(CH_3)_2C_6H_4NN^+$ deviate significantly from a straight line. If the data for the latter cation are excluded, the slope of this line, ρ, is 0.65 and the coefficient of determination, r^2, is 0.994. Although the good linear relationship observed for log K vs. $\sigma_p{}^+$ suggests that the interaction is primarily electrostatic, the absence of definite trends in the ΔH (or $T\Delta S$) values through the series indicates that a more involved explanation requiring further investigation is necessary to explain the observed trends.

The straight-line fit of data shown in Figure 2 predicts that log K for the interaction of p-$N(CH_3)_2C_6H_4NN^+$ with 18C6 should be approximately 1.4, whereas the measured value is 0.9 ± 0.1. Although log K was relatively small and therefore difficult to determine as accurately as with the other diazonium cations studied (Table II, footnote e), it is well below the expected value. Deviations of this type for other systems with extremely low $\sigma_p{}^+$ values are known.[14]

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