

Thermodynamics of Formation of 18-Crown-6 Complexes with Arenediazonium and Anilinium Salts in Methanol at 25 °C

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Summary Binding of 18-crown-6 to arenediazonium cations, which has previously been shown to stabilize the cation against decomposition, is found to be very sensitive to electronic factors and much more sensitive to steric factors than is binding to corresponding anilinium cations.

values for formation of 18-crown-6 complexes with simple and substituted arenediazonium and anilinium salts in methanol at 25 °C by titration calorimetry.⁴ We find that complexation of arenediazonium salts is much more sensitive to steric factors due to aromatic substitution than is that of anilinium salts, and is very sensitive to electronic factors as well.

BARTSCH and his co-workers¹ reported that the rates of thermal decomposition of *p*-*t*-butylbenzenediazonium ion in organic solvents and of photochemical decomposition of benzenediazonium ion in the solid phase are significantly reduced by addition of an appropriate crown ether. The cyclic polyether 18-crown-6 was found to be a much more effective inhibitor than 15-crown-5 or triglyme presumably because the cavity dimensions in this macrocycle allow insertion of the diazonium group as illustrated in the Figure (a). The formation of such arenediazonium-crown ether complexes has been verified by solubilization n.m.r. experiments² and by i.r. spectroscopy.³ As part of a systematic investigation of the bonding of organic cations to crown ethers, we have determined $\log K$, ΔH , and $T\Delta S$

The Table lists $\log K$, ΔH , and $T\Delta S$ values for the interaction of 18-crown-6 with the diazonium and anilinium cations studied. The values reported represent the average of results from 3–6 independent determinations. As the $\log K$ data illustrate, binding of 18-crown-6 to diazonium ions is invariably weaker than is that to corresponding anilinium ions. This difference is due to much stronger entropic opposition to reaction in the diazonium case, an observation which will be discussed in a future publication.

X-Ray crystallographic data⁵ show that NH_4^+ binds to dicyclohexano-18-crown-6 *via* hydrogen bonds to the ether oxygen atoms. It is likely that the anilinium ion behaves similarly sitting on top of the macrocycle [Figure (b)] rather than inserting itself into the ring cavity as does the diazonium ion³ [Figure (a)]. Thus, the diazonium

TABLE. $\log K$, ΔH , and $T\Delta S$ for formation of 18-crown-6 complexes with arenediazonium and anilinium salts in methanol at 25 °C.

Cation	Anion	$\log K$	ΔH^a	$T\Delta S^a$
Ph-N \equiv N ⁺	BF ₄ ⁻	2.37 ± 0.04	-14.0 ± 0.5	-10.8
<i>p</i> -MeC ₆ H ₄ -N \equiv N ⁺	BF ₄ ⁻	2.26 ± 0.02	-10.03 ± 0.28	-6.95
<i>o</i> -MeC ₆ H ₄ -N \equiv N ⁺	BF ₄ ⁻	b	b	—
<i>oo'</i> -Me ₂ C ₆ H ₃ -N \equiv N ⁺	BF ₄ ⁻	c	c	—
<i>p</i> -Et ₂ NC ₆ H ₄ -N \equiv N ⁺	BF ₄ ⁻	d	d	—
PhNH ₃ ⁺	Br ⁻	3.80 ± 0.03	-9.54 ± 0.14	-4.36
<i>p</i> -MeC ₆ H ₄ NH ₃ ⁺	Br ⁻	3.82 ± 0.04	-9.92 ± 0.22	-4.71
<i>mm'</i> -Me ₂ C ₆ H ₃ NH ₃ ⁺	I ⁻	3.74 ± 0.02	-9.07 ± 0.06	-3.97
<i>o</i> -MeC ₆ H ₄ NH ₃ ⁺	Br ⁻	2.86 ± 0.03	-7.59 ± 0.15	-3.69
<i>oo'</i> -Me ₂ C ₆ H ₃ NH ₃ ⁺	Br ⁻	2.00 ± 0.05	-5.65 ± 0.27	-2.92

^a kcal mol⁻¹. ^b No measurable heat other than heat of dilution, indicating that $\log K$ is very small and/or ΔH is close to zero. ^c Cation decomposes too rapidly to allow measurement. ^d Heat is produced, but quantity is too small to allow calculation of thermodynamic parameters.

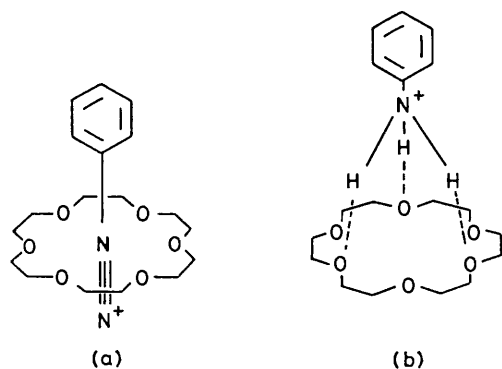


FIGURE. The structures of 18-crown-6 complexes of the benzenediazonium ion (a) and the anilinium ion (b).

group brings the entire aromatic system closer to the macrocyclic ligand in the complexed form than does an ammonium group. For this reason, one would expect a larger decrease in complex stability as a result of *ortho*-substitution on the benzene-diazonium ion than on the anilinium ion since such substitution would more effectively

block the approach of the substituted diazonium cation to the ligand. The data in the Table support this idea. Specifically, the addition of just one *ortho* methyl group to the benzenediazonium ion effectively eliminates reaction altogether, whereas the stability of the anilinium complex drops approximately one $\log K$ unit upon each addition of a methyl group adjacent to the ammonium group.

Electronic factors are also found to have considerable effect on the binding of 18-crown-6 to arenediazonium salts. As illustrated in the Table, addition of a strongly electron donating group like NEt_2 *para* to the diazonium group is sufficient to cause almost total loss of stability of the complex. This is presumably due to the delocalization of positive charge away from the diazonium group.

Since the stability of arenediazonium-18-crown-6 complexes is so sensitive to steric and electronic effects, this crown ether would be expected to stabilize those sterically unhindered diazonium cations which have an appreciably localised +ve charge on the nitrogen atoms similar to those used by Bartsch.¹

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⁵ B. L. Haymore, unpublished results.