

STUDIES OF CROWN ETHER COMPLEXES
ARYLDIAZONIUM ION COMPLEXES

Jostein Krane* and Tore Skjetne

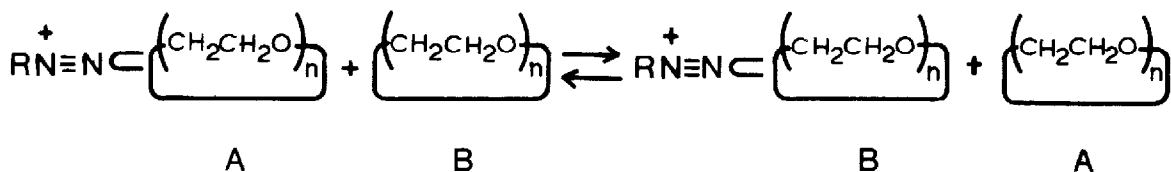
Kjemisk Institutt, NLHT, Universitetet i Trondheim,
N-7000 Trondheim, Norway

Abstract: DNMR studies show that for complexation of aryldiazonium salts 21-crown-7 is the preferred host.

Complex formation of aryldiazonium ions by macrocyclic polyethers (crown ethers) has been shown by spectroscopic,¹ kinetic² and calorimetric³ studies. Studies of aryldiazonium ion complexations by acyclic polyethers⁴ (glymes) and polyethylene glycols and their ethers⁵ have just recently been published.

Gokel and his coworkers^{6,7} have put the crown ether 18-crown-6 to synthetic use by designing new syntheses of aryl iodides, aryl bromides and unsymmetrical biaryls from aryldiazonium salt reactions in solvents of low polarity. The 18-crown-6 was used to phase transfer aryldiazonium tetrafluoroborates into chloroform and benzene.

We here report studies that clearly demonstrate the ring size effect on the decomplexation barrier in a process most simply described as:⁸



n=6,7,8

Variable temperature NMR spectroscopy of solutions containing

equimolar amounts of crown ether and the 1:1 complex (i.e. molar ratio of crown to salt of 2:1) has proved to be an extremely valuable technique in the investigation of the kinetics of decomplexation of ligands. In this approach, signals for complexed and uncomplexed crown ether become evident in the spectra under conditions of slow exchange provided that there is a sufficient shift dispersion between the two species.

When a solution in CHCl_2F containing two equivalents of crown ether per equivalent of p-methylbenzenediazonium tetrafluoroborate salt is cooled, the single ^1H or ^{13}C line of the crown ether starts to broaden and then splits into two sharp lines of equal intensities. The coalescence temperature, T_c , the rate constant⁹ at that temperature and the corresponding calculated activation free energy¹⁰ for the decomplexation barrier of the macrocyclic polyethers 18-crown-6, 21-crown-7 and 24-crown-8 are included in Table 1.

Table 1. a)

Host	Ratio	T_c (K)	k (sec ⁻¹) ^{b)}	ΔG_c^\ddagger (kcal/mol) ^{c)}	
18-crown-6	p- $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$	2:1	198	24	10.1
21-crown-7	"	2:1	221	43	11.1
24-crown-8	"	2:1	181	19	9.3

a) Data obtained from ^{13}C NMR at 25.05 MHz

b) Calculated according to ref.9

c) Calculated according to ref.10

These results clearly demonstrate that 21-crown-7 is the preferred host for complexation of diazonium ions. In this connection it is quite interesting to note the result obtained by Bartsch and Juri,⁴ that heptaglyme gave the most stable complex with p-tert-butylbenzenediazonium tetrafluoroborate over hexaglyme and octaglyme.¹¹

Another important observation is that both the ^1H and the ^{13}C resonances in the complexed crown ether ligands remain a single line in the slow exchange spectrum, which means that the conformational processes averaging protons and carbons are still fast on the NMR time scale. The decomplexation barrier for the crown complexes studied exceeds by far any conformational barrier within the ligands.¹²

The calorimetric studies by Izatt et al.³ on formation of 18-crown-6 complexes with aryldiazonium salts in methanol at 25 °C revealed strong steric and electronic effects. We have investigated the decomplexation barrier for a series of substituted aryldiazonium salts, and the results are shown in Table 2.

Table 2. a)

Host	Guest	Ratio	T _c (K)	k(sec ⁻¹)	ΔG _c [‡] (kcal/mol)
18-crown-6	C ₆ H ₅ [‡] N ₂ PF ₆ ⁻	2:1	198	24	10.1
"	p-FC ₆ H ₄ [‡] N ₂ BF ₄ ⁻	2:1	193	19	10.0
"	p-MeC ₆ H ₄ [‡] N ₂ BF ₄ ⁻	2:1	194	20	10.0
"	p-NO ₂ C ₆ H ₄ [‡] N ₂ BF ₄ ⁻	2:1	193	16	10.0
"	m-NO ₂ C ₆ H ₄ [‡] N ₂ BF ₄ ⁻	2:1	191	18	9.9
"	p-N(C ₂ H ₅) ₂ C ₆ H ₄ [‡] N ₂ BF ₄ ⁻	2:1	-	-	-
"	p-OC ₆ H ₄ [‡] N ₂ BF ₄ ⁻	2:1	-	-	-

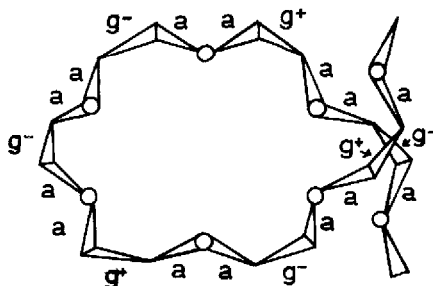
a) Data obtained from ¹³C NMR. Solvent: CHCl₂F.

As can be seen from this table, the decomplexation barrier is not particularly dependent on charge changes on the [‡]N≡N group in those cases where we were able to detect a decomplexation barrier. On the other hand, it might be premature to draw a definite conclusion from this preliminary investigation. In two extreme cases, with $\overset{\ominus}{\text{O}}\text{C}$ and $\overset{\ominus}{\text{N}}(\text{Et})_2$ as para substituents, we were not able to determine a decomplexation barrier with our 23.5 kG magnet. Either this is due to a small shift dispersion between the complexed and uncomplexed crown ether, or very low barriers to decomplexation exist. In both events, high field NMR investigations at still lower temperatures might give an answer to the problem encountered.

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11. These authors claim that examination of a CPK space-filling model reveals that a "cyclic" structure for heptaglyme in which all eight oxygen atoms lie in a plane, can exist without causing serious van der Waals repulsions or bond angle strain. CPK models may be quite deceitful because they can easily be assembled in erroneous conformations if proper attention is not paid to obtaining realistic torsional angles. We tentatively propose a model as depicted in the figure for heptaglyme in the complexed form.



This model has the advantage that CCOC and COCC torsional angles are close to anti and the OCCO torsional angles are close to gauche, with alternating + and - signs, but requires adjustment of both internal and torsional angles to get a helical arrangement. The proposed model is in accordance with structural features revealed in the RbI complex of heptaethyleneglycol-bis(8-oxyquinoline) ether,¹³ except that in the diazonium complex only the two terminal oxygens in the heptaethyleneglycol fragment are on the same longitudinal circle on a spherical surface. If this is the optimum arrangement for the acyclic ligand in diazonium complexes, it is then easy to explain the lower stability constants for hexa- and octaglyme. Hexaglyme will give too small a cavity for the diazonium ion, and octaglyme will give steric repulsion between the phenyl ring in the diazonium ion and part of the ligand. Whatever the correct answer is, only an X-ray analysis will tell.

12. Below -130°C a conformational process averaging carbons in the complexed 18-crown-6 has become slow. The ^{13}C spectrum shows two resonances for the ligand, J. Krane and T. Skjetne, unpublished results.
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