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RATES OF DEDIAZONIATIONS OF ARENEDIAZONIUM IONS COMPLEXED WITH 18-, 21- AND 24-MEMBERED CROWN ETHERS[1]

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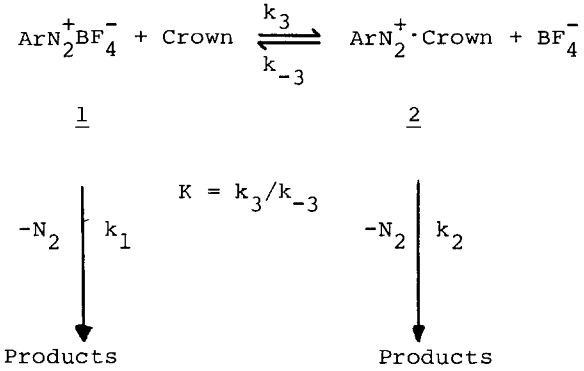
Abstract: The evaluation of the kinetics of dediazoniation of benzenediazonium tetrafluoroborate and p-chlorobenzenediazonium tetrafluoroborate in 1,2-dichloroethane at 50°C in the presence of 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8 demonstrates that the rate constant for the dediazoniation within the complex is smallest, and the equilibrium constant for complex formation is largest for the complex with 21-crown-7.

Gokel and Cram[3] first observed the interaction of arenediazonium ions with crown ethers and the non-reactivity of the complexed diazonium salts in diazo coupling reactions. Bartsch *et al.*[4,5] investigated the markedly enhanced thermal stability in 1,2-dichloroethane of the complex of *p*-*tert*-butylbenzenediazonium tetrafluoroborate with 18-crown-6 and 40 other macrocyclic multidentate compounds relative to the uncomplexed diazonium salt. After the evaluation of the dediazoniation kinetics with varying concentrations of 18-crown-6 according to the following Scheme, they concluded[4] that $k_2 \cong 0$, or at least $k_1 > 100\ k_2$. Their results[5] also indicated maximum complexation with 21-crown-7.



The same conclusion was reached by Krone and Skjetne[6] who studied the dynamic NMR spectra of complexes of p-methylbenzenediazonium ions with 18-crown-6, 21-crown-7 and 24-crown-8 in dichlorofluoromethane. They determined the decomplexation rate constants k_{-3} which, in agreement with Bartsch's results, also indicated that 21-crown-7 is the preferred host for the complexation of arenediazonium salts.

The equilibrium constants (K) for the complexation of o-, m-, and p-substituted benzenediazonium salts with 18-crown-6 were determined independantly by Kuokkanen and Virtanen[7] in 1,2-dichloroethane and by Hashida and Matsui[8] and Izatt *et al*. in methanol. The rate constant for the dediazoniation of the 18-crown-6 complex 2, k_2, was found[7] not to be zero, but approximately 1% of the rate of the uncomplexed diazonium salt 1, k_1, (about 15% for the p-Cl compound).

In this communication we report the first determination of the rate constants k_2 for the dediazoniation of complexed diazonium ions and of the equilibrium konstants K as a function of the ring size of the crown ether. Specifically, we investigated the dediazoniation kinetics of benzenediazonium and p-chlorobenzenediazonium tetrafluoroborates in the presence of varying amounts of 18-crown-6, 21-crown-7 and dicyclohexano-24-crown-8 in 1,2-dichloroethane. The experimental technique first introduced by Bartsch *et al*.[4] and further developed by Kuokkanen and Virtanen[7] was used.

Rate Constants of Dediazoniation of Arenediazonium Ions (k_1 and k_2) and Complex Formation Constants (K) in 1,2-Dichloroethane at 50°C.

Diazonium salt	Crown ether	$K(l\cdot mol^{-1})$	$k_1 (s^{-1})$	$k_2 (s^{-1})$
$C_6H_5N_2^+BF_4^-$	18-crown-6[10]	$6.05x10^4$	$1.17x10^{-3}$	$0.03x10^{-3}$
	21-crown-7	$6.15x10^5$		$0.01x10^{-3}$
	dicyclohexano-24-crown-8	$3.37x10^4$		$0.10x10^{-3}$
$\underline{p}$-$ClC_6H_4N_2^+BF_4^-$	18-crown-6[10]	$7.72x10^4$	$2.35x10^{-6}$	$0.23x10^{-6}$
	21-crown-7	$1.54x10^5$		$0.04x10^{-6}$
	dicyclohexano-24-crown-8	$2.05x10^4$		$0.39x10^{-6}$

The results in the Table indicate that, among the crown ethers studied, 21-crown-7 produces maximum complexation of arenediazonium ions (largest K), as well as maximum stabilization towards thermal dediazoniation in the complex (smallest k_2). 18-Crown-6 is the second best complexing agent, and dicyclohexano-24-crown-8 the poorest. The dediazoniation rate, k_2, of the benzenediazonium salt/decyclohexano-24-crown-8 complex is 10% of the dediazoniation rate of the uncomplexed diazonium ion, compared to ca. 3% for the 18-crown-6 complex and ca. 1% for the 21-crown-7 complex.

One might argue that the complexed diazonium ions are completely stable (k_2=0) and that the lower rates of dediazoniation of the complexed diazonium ions are due to a slow decomplexation to the diazonium ion pair $\underline{1}$ (rate constant k_{-3}) which then decomposes in the usual way. This mechanism can not be correct as Krane and Skjetne[6] found that decomplexation is very fast (k_{-3}=19 to 43 s^{-1} at -92°C to -52°C). $\underline{1} \rightleftharpoons \underline{2}$ can therefore be treated as a fast equilibrium[11] prior to the rate determining step. Bartsch's[4] and Kuokkanen and Virtanen's[7] treatment of the kinetic data is therefore appropriate.

We plan to investigate the mechanism of the decreased rates of dediazoniations of crown ether-complexed arenediazonium salts relative to the uncomplexed salts. At present we can say only that there are no linear relationships between k_2 and K for the three crown ether complexes with both the arenediazonium ions we have studied. There are also no such relationships between k_1 and k_2 for substituted arenediazonium salt/crown ether systems[7]. This indicates a dediazoniation mechanism for complexed diazonium ions which is different from that of the free diazonium ion which we investigated in detail in recent years[12].

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10. Our values for k_1, and for k_2 and K in the presence of 18-crown-6, differ from those reported by Kuokkanen and Virtanen[7], but the differences are not large and may well lie within experimental error.
11. Using the known equilibrium constant for complex formation[7] and the decomplexation rate constant[6] a minimum value for the complexation rate, $k_3 > 6 \times 10^5$ l mol^{-1} s^{-1}, can be estimated for the complexation of p- methylbenzenediazonium salt with 18-crown-6 in 1,2-dichloroethane, or dichlorofluoromethane as solvents.
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