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COMPLEXATION OF ARYLDIAZONIUM IONS BY GLYMES

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The complexation of aryldiazonium ions by macrocyclic polyethers (crown ethers) has been demonstrated by spectroscopic,[1] kinetic,[2] and calorimetric studies.[3] One to one complexes of aryldiazonium salts and crown ethers have been isolated.[2,4] We now report studies of aryldiazonium ion complexation by acyclic polyethers (glymes).

Considerable attention is currently being focused upon the use of glymes and other oligoethylene glycol ethers, $CH_3O(CH_2CH_2O)_nCH_3$, for the complexation of alkali and alkaline earth cations and as phase transfer catalysts in reactions involving salts of these cations.[5-10] In order to examine the interactions of aryldiazonium salts with acyclic polyethers, the influence of individual glymes[11] from diglyme to decaglyme and the dimethyl ether of Carbowax 1000 upon the thermal decomposition of p-tert-butylbenzendiazonium tetrafluoroborate (1) in 1,2-dichloroethane was measured.

Kinetics of the thermolysis of 1 in 1,2-dichloroethane at 50.0°C in the absence and presence of ten equivalents of individual glymes were followed by ultraviolet spectroscopy. In the absence of glyme, 1 exhibited an absorption maximum at 285 nm. In the presence of ten equivalents of glyme, the absorption maximum usually was shifted to somewhat shorter wavelengths (see Table). The reaction products are transparent in this region.[12] Excellent first-order kinetic plots covering at least two half lives of the reaction were obtained.

Observed first order rate constants for the thermal decomposition of 1 in the absence and presence of ten equivalents of glyme are recorded in the Table. In agreement with previous studies of the effects of crown ethers upon the thermolysis of 1,[2] the rate of thermal decomposition is lower in the presence of glymes.

The rate retardations may readily rationalized if complexation of 1 by a glyme converts the diazonium salt into an unreactive, complexed form (Equation). Strong precedent for this

$$ArN_2^+BF_4^- + \text{Glyme} \underset{}{\overset{K}{\rightleftharpoons}} \text{Complex} \qquad \text{(Equation)}$$

$$ArN_2^+BF_4^- \xrightarrow{k_1} \text{Products}$$

mechanism is derived from the interaction of crown ethers with 1 under identical reaction conditions.[2]

The observed rate data may be used to evaluate K, the complexation constant, since

$K = (k_1 - k_{obs})/k_{obs}[Glyme]$, where k_1 is the rate constant for the thermolysis of 1 in the absence of glyme and [Glyme] in the initial glyme concentration. Complexation constants for the interactions of ten glymes with 1 in 1,2-dichloroethane at 50.0°C are listed in the Table and are graphically presented in the Figure.

Table. Observed First Order Rate Constants for the Thermal Decomposition of 1[a] in 1,2-Dichloroethane at 50.0°C.

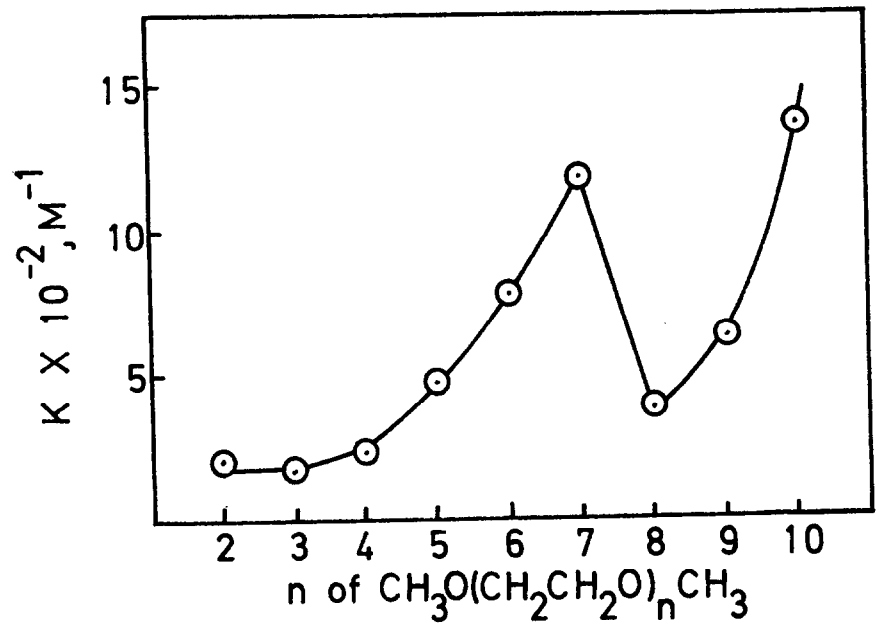
Glyme[b]	λ_{max}, nm[c]	$k_{obs} \times 10^4$, sec^{-1}[d]	$K \times 10^{-2}$, M^{-1}
None	285	2.48	--
Diglyme	284	2.22	2.00
Triglyme	282	2.28	1.71
Tetraglyme	285	2.18	2.36
Pentaglyme	280	1.94	4.78
Hexaglyme	280.5	1.71	7.71
Heptaglyme	280.5	1.47	11.8
Octaglyme	281.5	2.03	3.81
Nonaglyme	281.5	1.81	6.32
Decaglyme	278	1.38	13.6
Dimethyl Ether of Carbowax 1000	276	0.92	29.0

[a]Initial [1] = 5.84×10^{-5} M. [b]Initial [Glyme] = 5.84×10^{-4} M. [c]Measured diazonium ion absorption maximum. [d]Estimated maximum error is 2% to the rate constant.

The value of K is essentially constant for diglyme, triglyme, and tetraglyme. The monotonic enhancements in K for pentaglyme, hexaglyme, and heptaglyme are consistent with an increasing ability of the glyme to assume a pseudo cyclic structure. Examination of CPK space-filling models reveals that a cyclic structure for heptaglyme in which all eight oxygen atoms lie in a plane can be attained without serious Van der Waals repulsions or bond angle strain. For octaglyme, the models indicate serious repulsions and strain in any conformation which would allow the nine oxygen atoms to be planar within a pseudo cyclic cavity. The anticipated poorer complexation with octaglyme than heptaglyme is readily evident from the complexation data in the Table and Figure. After the reduction in K noted for octaglyme, an increasingly efficient complexation with nonaglyme and decaglyme indicates the introduction of a supplemental factor for the longer glymes. The CPK models reveal that for nonaglyme and decaglyme seven or eight oxygens may form a pseudo cyclic cavity with the remaining oxygens located in an arm which passes over one face of the cavity. Thus, when complexed with 1 the longer glymes appear to assume conformations that are not only crown ether-like, but also cryptand-like.

It would be desirable to examine the complexation of 1 by individual glymes even larger than decaglyme. Unfortunately, these higher glymes are not readily available. In order to indicate the upper limit to be expected for complexation of aryldiazonium ions by glymes, the

Figure. Complexation Constants for Interactions of 1 with Glymes in 1,2-Dichloroethane at 50.0°C



dimethyl ether of Carbowax 1000, $CH_3O(CH_2CH_2O)_{22-23}CH_3$, was prepared. The complexation constant calculated for this glyme mixture is approximately twice as great as that found for decaglyme.

The complexation constant for the interaction of 18-crown-6 with 1 in 1,2-dichloroethane[2] at 50.0°C is 1.56×10^4 M^{-1}. Comparison of K values for pentaglyme and 18-crown-6 reveals a macrocyclic effect of approximately thirty for the complexation of aryldiazonium ions by polyethers. In a similar comparison of tert-butylammonium thiocyanate complexation by pentaglyme and 18-crown-6 in chloroform at 24°C, a macrocyclic effect of 18,700 has been reported.[13] Thus, the magnitude of the macrocyclic effect is demonstrated to be highly dependent upon the nature of the cationic species being complexed.

The complexation constant for 18-crown-6 is only about five fold greater than that for the dimethyl ether of Carbowax 1000. This presents the possibility of using the less expensive glyme mixture in reactions of aryldiazonium salts which utilize 18-crown-6 as a phase transfer catalyst.[14-16] Investigation of this possibility is in progress.

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References and Notes

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11. Diglyme, triglyme, and tetraglyme were obtained from Aldrich Chemical Company and were purified by distillation from lithium aluminum hydride. The remaining individual glymes were purchased from Parish Chemical Company, Provo, Utah and were used as received. Carbowax 1000 was obtained from Applied Science Laboratories, State College Pennsylvania, and was methylated by reaction with dimethyl sulfate and powdered NaOH in methylene chloride.
12. Relative yields of products from the thermolysis of 1.0×10^{-2} M 1 in 1,2-dichloroethane at 50.0°C in the presence of 1.0×10^{-1} M heptaglyme were determined by gas chromatography to be: 64% of p-chloro-tert-butylbenzene, 32% of p-fluoro-tert-butylbenzene, and 4% of tert-butylbenzene. Under the same conditions but in the absence of glyme, the relative product yields were 66% of p-chloro-tert-butylbenzene and 34% of p-fluoro-tert-butylbenzene.
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