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COMPLEXATION OF ARYLDIAZONIUM IONS BY POLYETHYLENE GLYCOLS AND THEIR ETHERS[1]

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Summary. Complexation constants for interactions of p-tert-butylbenzenediazonium tetrafluoroborate with polyethylene glycols and their mono- and dimethyl ethers in 1,2-dichloroethane are reported. For polyethylene glycols of molecular weights 1000 and 1500 and their dimethyl ethers complexation constants with the aryldiazonium ion are 12-18% of that for the crown ether 18-crown-6.

Complexation of aryldiazonium salts with crown ethers markedly modifies the usual solubility properties and reactivity of this important class of organic reagents. Thus, in the presence of suitable crown ethers, ionic arenediazonium salts may be solubilized in non-polar organic solvents such as chloroform.[3] The crown ether 18-crown-6 has been utilized as a phase transfer catalyst for reactions of aryldiazonium salts in chloroform[5] and benzene.[6] In addition to the solubilization phenomenon, crown ether complexation of arenediazonium salts produces thermal[6] and photochemical[7] stabilization, as well as diminished electrophilic reactivity.[8,9]

Although the initial solubilization studies of Gokel and Cram[3] indicated that the cyclic polyether structure was requisite for efficient aryldiazonium ion complexation, we have recently observed that substantial complexation may be achieved with glymes.[10] In the investigation, complexation constants for the association of p-tert-butylbenzenediazonium tetrafluoroborate with individual glymes from diglyme through decaglyme in 1,2-dichloroethane were determined. The complexation constant measured for the strongest interacting glyme, decaglyme, was approximately one tenth of that for the crown ether 18-crown-6.

This result indicates that appropriate acyclic polyether compounds might provide the modified solubility and reactivity of aryldiazonium salts previously obtained with crown ethers. This possibility has important economic ramifications since a variety of acyclic polyether compounds are readily-available, industrial products of very low cost compared with crown ethers. For these reasons, an investigation of aryldiazonium cation complexation by polyethylene glycols (PEG's) and their mono- and dimethyl ethers was undertaken.

Kinetics of the thermal decomposition[11] of p-tert-butylbenzenediazonium tetrafluoroborate, 1, in 1,2-dichloroethane at 50.0°C in the absence and presence of ten equivalents of polyoxygen compound were followed by measuring the rates of disappearance of absorption due to 1 at 275-285 nm. Linear first-order kinetic plots covering at least two half lives were obtained. Observed first-order rate constants for the thermolysis of 1 in the presence of polyethylene glycol (PEG, with average molecular weights of 300, 600, 1000, and 1500[12]), polyethylene glycol monomethyl ethers (PEG-MME, with average molecular weights of 350, 550, and 750[13]), and polyethylene glycol dimethyl ethers (PEG-DME, prepared by methylation of the corresponding glycols[14]) are listed in the Table. In agreement with the previous studies of the effects of crown ethers[6] and pure glymes[10] upon the thermolysis of 1, the rates of thermal decomposition are less in the presence of PEG's and their ethers.

From the rate data, complexation constants K for the association of 1 with the polyoxygen compounds (Equation) were calculated.[10] These values are also listed in the Table.

$$\mathrm{ArN_2{}^+BF_4{}^-} + \text{Polyoxygen Compound} \xrightleftharpoons{K} \text{Complex} \qquad \text{(Equation)}$$

Table. Observed First-Order Rate Constants for the Thermal Decomposition of 1[a] in the Presence of PEG and PEG Derivatives and Complexation Constants for the Association of 1 with PEG and PEG Derivatives in 1,2-Dichloroethane at 50.0°C.

Polyoxygen Compound[b]	Average Number of (CH_2CH_2O) Units	$k_{obs}{}^c \times 10^4$, sec^{-1}	$K \times 10^{-2}$, M^{-1}
None	--	2.51	--
PEG 300	6.4	1.76	7.30
PEG 600	13.2	1.23	17.8
PEG 1000	22.3	1.09	22.3
PEG 1500	33.7	1.01	25.4
PEG-MME 350	7.2	1.57	10.2
PEG-MME 550	11.8	1.24	17.5
PEG-MME 750	16.3	1.15	20.2
PEG-DME 300[d]	6.4	1.59	9.91
PEG-DME 600	13.2	1.31	15.7
PEG-DME 1000	22.3	0.90	30.6
PEG-DME 1500	33.7	1.15	20.2

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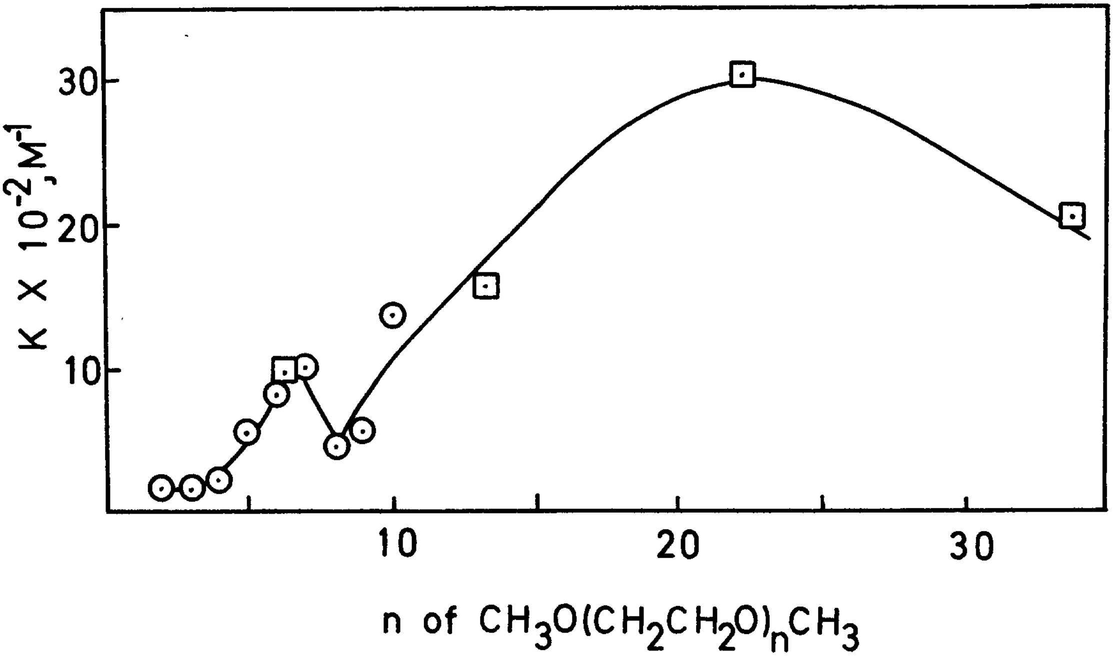
[a] Initial [1] = 5.84×10^{-5} M. [b] [Polyoxygen Compound] = 5.84×10^{-4} M. [c] Estimated maximum error is 2% of the rate constant. [d] [PEG-DME 300] = 5.31×10^{-4} M.

In the Figure, complexation constants for the association of polyethylene glycol dimethyl ethers (squares) with 1 are compared with those for individual glymes from diglyme to decaglyme (circles). The point for PEG-DME 300 closely correlates with the pattern established for the individual glymes. Therefore, the points for PEG-DME 600, 1000, and 1500 may be used to extend the previously-reported[10] relationship to higher molecular weight glymes. The enhanced complexation observed with the higher molecular weight glyme mixtures apparently reaches a maximum with PEG-DME 1000. Further lengthening of the polyether chain to PEG-DME 1500 produces less efficient complexation.

The complexation constant for the interaction of the crown ether 18-crown-6 with 1 in 1,2-dichloroethane at 50.0°C is 1.71×10^4 M^{-1}. This association is only about five-fold greater than that observed with PEG-DME 1000. This result further underscores the low

Figure. Complexation Constants for Interactions of 1 with Pure Glymes (Circles) and Polyethylene Glycol Dimethyl Ethers (Squares) in 1,2-Dichloroethane at 50.0°C.



macrocyclic effect[10] for polyethers in complexation of aryldiazonium ions.

Recently, PEG-DME's were utilized as phase transfer catalysts in reactions of potassium salts with organic substrates.[15] In the publication, no mention was made of the relative efficiencies of the corresponding PEG's themselves. In the absence of such information, one might infer that methyl end groups are necessary. Since PEG-DME's must be synthesized, whereas PEG's and PEG-MME's are commercially-available, information concerning the effect of end group variation would have considerable practical importance.

The complexation constant data in the Table may be used to assess the influence of end groups of the polyoxygen compound upon the efficiency of complexation with 1. Comparison of the complexation constants reveals little influence of the end groups upon the strength of complexation. Complexation efficiency is apparently determined almost completely by the number of $-(CH_2CH_2O)-$ units in the polyoxygen compound.

Because of the small macrocyclic effect and the independence of complexation efficiency from end group identity, it should be possible to substitute inexpensive PEG's for crown ethers as solubilizing and stabilizing agents for aryldiazonium salts. In this paper, we have demonstrated that PEG 1000 and PEG 1500 provide substantial thermal stabilization of aryldiazonium ions through complexation. In the following communication, the capacity of PEG 1000 to function as a phase transfer catalyst in aryldiazonium salt reactions is reported.[16]

References and Notes

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(11) The thermolysis of 1 in 1,2-dichloroethane at 50.0°C produced *p*-*tert*-butylchlorobenzene and *p*-*tert*-butylfluorobenzene.[10] The relative amounts of these products were essentially unchanged when the decomposition of 1 was conducted in the presence of heptaglyme or 18-crown-6. It is assumed that the products are also unchanged by the presence of polyethylene glycol and its derivatives.

(12) Polyethylene glycols 600, 1000, and 1500 were from Applied Science Laboratories. Polyethylene glycol 300 was from Fluka. All were used as received.

(13) Polyethylene glycol monomethyl ethers (Carbowax 350, 550, and 750) were generously provided by Union Carbide Corporation, South Charleston, West Virginia.

(14) Dimethyl sulfate was slowly added to a vigorously stirred mixture of a polyethylene glycol and powdered KOH in CH_2Cl_2 at 0°C. After the addition was completed, the mixture was refluxed for one hour, filtered, and the CH_2Cl_2 solution was evaporated *in vacuo*. The resulting product was dissolved in a minimum amount of CH_2Cl_2 and absorbed on the top of an alumina column. Elution with Et_2O and removal of the Et_2O *in vacuo* gave the polyethylene glycol dimethyl ether which had PMR and IR spectra consistent with the proposed structure.

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