Acknowledgment. The authors gratefully acknowledge the support of this research by the National Science Foundation, CHE 7905890.

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Received September 11, 1979

The Remarkable Catalytic Power of Glymes in Ester Aminolysis Carried Out in Nonpolar Media

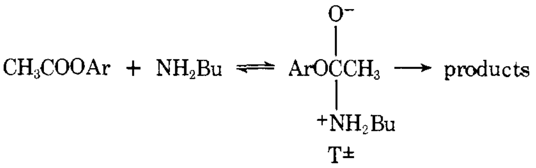
Sir:

Recently we reported[1] that crown ethers with pyridine rings incorporated into their macrocyclic arrays are very effective catalysts in the butylaminolysis of *p*-nitrophenyl acetate (*p*-NPA) in chlorobenzene. In an effort to elucidate the nature of the observed catalysis, we decided to systematically compare the catalytic efficacies of simple (unsubstituted) crown ethers (hereinafter referred to as crowns) with the catalytic efficacies of their open-chain analogues, oligo(ethylene glycol dimethyl ethers), viz., glymes.

Crowns are generally known[2] to be better complexing agents than glymes, and might therefore be expected to be better aminolysis catalysts as well. It is known,[3] for example, that in binding *tert*-butylammonium ion, 18-crown-6 is a better complexing agent than pentaglyme by a factor of $>10^4$. Thus the enforced convergence of binding sites (oxygens) provided by the crown results in an increase in stabilization in the complex of ~5.9 kcal/mol at 24 °C. It might be anticipated that a similar macrocyclic effect[2] should be observed for catalysis of reactions (such as aminolysis) involving ammonium-ion-like intermediates. Much to our surprise the glymes have turned out to better catalysts than the corresponding crowns! In addition, we have found that crowns with pyridine rings incorporated into their macrocyclic arrays were not as catalytically effective as unsubstituted crowns.

These results lead us to suggest that a flexible polyether species which can adapt is a better catalyst than a more rigid polyether which does not have the correct features for catalysis. The "guest" transition-state structure whose stabilization leads to catalysis prefers a "host" polyether with sufficient rotational freedom to adopt a conformation that results in catalysis. For macrocycles, this rotational freedom exists only in the larger rings.

Ester aminolysis carried out in a nonpolar solvent is believed[4,5] to involve the initial formation of a tetrahedral intermediate, T±, whose breakdown (in one or more steps to form product) is rate determining. Catalysis of the reaction by bases appears[6] to involve stabilization of a transition-state structure resembling T± by a catalyst, possibly via a hydrogen-bonded complex. Hydrogen bonding to or transfer of an ammonium proton in T± appears[6] to facilitate the expulsion of ArO⁻. This type of catalytic role seems reasonable for crown and glyme catalysts in the light of the well-known[2] ability of crowns and glymes to complex with a wide variety of cations,[7-12] including ammonium ions.[2,3,8,11,12] However, secondary ammonium species such as T± are not complexed[12] well by 18-crown-6.



$$\mathrm{CH_3COOAr + NH_2Bu \rightleftharpoons ArO\overset{O^-}{\underset{^+NH_2Bu}{C}}CH_3 \longrightarrow products}$$

T±

Table I. Catalytic Rate Constants for Butylaminolysis of *p*-NPA in Chlorobenzene at 25 °C

catalyst	$k' \times 10^3$ ($M^{-2}\,s^{-1}$)	k'_{rel}	$-RT \ln k'_{rel}$ (kcal/mol)[a]
1, *n* = 2	25 ± 6[b]	1.0	0.00
n = 3	123 ± 7	4.9	−0.94
n = 4	280 ± 20	11	−1.43
n = 5	340 ± 40	14	−1.55
n = 7	550 ± 10	22	−1.83
n = 8	590 ± 30	24	−1.87
n = 11	920 ± 30	37	−2.14
n = 22.3[c]	1,900 ± 100	76	−2.57
2, n = 2	16 ± 7	0.52	0.39
n = 4	70 ± 8	2.8	−0.61
n = 5	130 ± 10	5.2	−0.98
n = 6	220 ± 20	8.8	−1.29
n = 7	340 ± 20	14	−1.55
3, n = 5[d]	7 ± 2	0.29	0.74
n = 6[d]	27 ± 2	1.1	−0.046
n = 7[d]	62 ± 1	2.5	−0.54
4, n = 10[d]	210 ± 3	8.4	−1.26
n = 12[d]	290 ± 4	12	−1.45
n = 14[d]	430 ± 10	17	−1.69
dibenzo-18-crown-6[d]	34 ± 3	1.4	−0.18

[a] ΔΔ*G* for pure catalytic pathway relative to monoglyme. [b] Standard error. [c] Based on the average molecular weight of Carbowax 1000. See ref 7 for preparation of dimethyl ether. [d] Taken from ref 1.

The kinetics of the butylaminolysis of *p*-NPA in PhCl followed the rate law[1,6]

$$k_{\mathrm{obsd}} = k_0[\mathrm{amine}]^2 + k'[\mathrm{amine}][\mathrm{catalyst}]$$

at 25 °C, where k_{obsd} was the pseudo-first-order rate constant for the decomposition of *p*-NPA. In practice the appearance of *p*-nitrophenol (a product of the aminolysis) was followed spectrophotometrically rather than the disappearance of *p*-NPA. Values of k' were obtained from plots of $k_{\mathrm{obsd}}/[\mathrm{amine}]$ vs. [catalyst]. Usually five determinations were made at each of five different concentrations of catalyst. Glymes (**1**, *n* = 2-5, 11, 22), crown ethers (**2**, *n* = 2, 4-6), and crown ethers with one or two pyridine rings incorporated into their macrocyclic arrays (**3**, *n* = 5-7, and **4**, *n* = 9, 10, 12, 14; respectively) were compared as catalysts for this reaction.

Our results are summarized in Table I and Figure 1. Table I lists the values of k' measured for the species **1**-**4**, and Figure 1 is a plot of these catalytic rate constants as a function of the number of oxygens, *n*, in the catalytic species. This plot is definitely linear through the glymes studied, and appears to curve gently upwards through the crowns. The significance of the curvature through the crowns and the linearity for the glymes is currently a topic for conjecture.[13] It is, however, interesting to speculate that the latter may arise from a linear relationship between the complexation constants of glymes complexed to some reactive intermediate (such as T±)[12b] and the number of oxygens per molecule in the glymes studied. In any case, the fact that the catalytic rate constants, on a per oxygen basis, decrease in going through the series **1** > **2** > **3** ≃ **4** seems to indicate to us that in order for a catalyst to be effective in this reaction it must have some conformational freedom. (The conformational freedom of the catalysts studied

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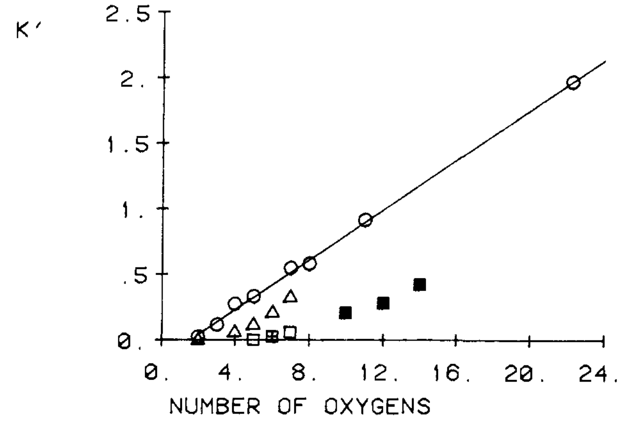
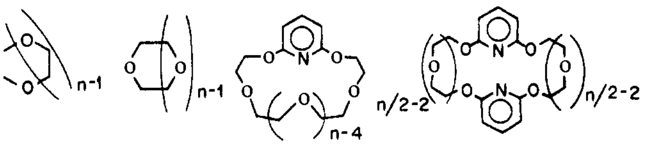


Figure 1. Plot of catalytic rate constant, k', vs. number of oxygens in the polyether catalyst: (○), **1**; (△), **2**; (□), **3**; (■), **4**; (+), dibenzo-18-crown-6.

would be expected to decrease in the same order, i.e., **1** > **2** > **3** ≃ **4**.)



1 **2** **3** **4**

In summary, catalysis of the aminolysis of *p*-NPA in PhCl shows an inverse macrocyclic effect. Catalysis is enhanced by flexible, less constrained polyethers and diminished by polyethers which are conformationally restricted.

Previous studies of catalysis by macrocycles have involved a different approach.[14] In these studies, one of the reactants has an ammonium ion and the other has a reacting group attached to a macrocycle. It is proposed that the binding of the ammonium ion and macrocycle serves to anchor the two reacting groups in close proximity which results in catalysis.

Our approach is to study catalytic effects of polyethers on reactions where ammonium ions are generated in the course of the reaction. The preferential affinity of the polyethers for the cationic intermediates and transition-state structures compared with that of the reactants will result in catalysis. Work is in progress in this laboratory to uncover the exact mechanistic nature of the observed catalysis and to explore other reactions potentially susceptible to polyether catalysis.

Acknowledgment. This research was supported by the Research Corporation. We thank Professor Richard A. Bartsch for generously providing us with a sample of dimethoxy Carbowax 1000. We also express our gratitude to the referees for their suggestions.

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(13) The curvature in the crown series may actually be a biphasic plot. The initial phase could represent catalysis resulting from a medium effect, while the latter phase could be catalysis by some type of complexation similar to the glymes. The "lag" in catalytic ability for the crowns and aromatic crowns is likely a direct indication of the ring size needed to achieve the flexibility required for catalysis.
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Received July 25, 1979

Photochemical Transformations. 27. Acid-Catalyzed Photosolvolytic Reactions and Rearrangements. Evidence for Heterolytic Photochemical Bond Cleavage[1]

Sir:

For some time, members of our research group have been interested in photochemically induced solvolyses and photo-Wagner-Meerwein rearrangements, reactions which presumably involve carbocationic intermediates.[2] One interesting question[2a] regarding such reactions is whether the ion pair leading to products is formed directly from the excited-state intermediate or whether it arises by intracomplex electron transfer within a radical pair formed initially. Put another way, is the initial photochemical reaction bond heterolysis or bond homolysis? Kropp and co-workers[3] have proposed that the *seriatim* process obtains, as a result of their studies of saturated alkyl iodides and bromides, where the carbon–halogen bond is the chromophore. Their ideas have been extended to benzyl derivatives,[4] where the aromatic ring is the chromophore, without additional evidence for or against this, as opposed to the idea of competing heterolytic and homolytic processes.[5,6] It is reasonable to assume that different processes are to be found with different substrates and under different conditions, and a conservative view[2a] may suggest that, at low separation distances, the distinction between radical and ion pairs may be blurred or may disappear.[7,8] We now report results that suggest that, for the system being studied at least, the initial photochemical process is not the formation of a classical radical pair.

It has been reported[2a] that direct irradiation with 254-nm light of **1**-Cl in aqueous acetonitrile gives photochemical "Wagner-Meerwein" rearrangement to a mixture of **2**-Cl and **3**-Cl, accompanied by photosolvolysis to give largely **2**-$NHCOCH_3$ and **2**-OH. Similar results were seen with **1**-Br. With the analogous systems *exo*- and *endo*-**4**, photochemical rearrangement gave **5**, and solvolysis produced *exo*-**4**-$NHCOCH_3$, when reaction was carried out in acetonitrile, followed by hydrolysis, or *exo*-**4**-$NHCOCH_3$ and *exo*-**4**-OH in aqueous acetonitrile.[2b] With **4**, photosolvolyses and rearrangements proceeded with X = chlorine, dichloroacetate, and methanesulfonate (good nucleofugal groups) but not with X = hydroxide or acetate. Irradiation of **4**-OH and **4**-OAc resulted instead in di-π-methane rearrangements to **6** species.[2b]

We now report results with **1**-OH, **1**-OAc, and **1**-OCOEt. Like the **4** analogues, when these compounds were irradiated

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