Protonation of Macrocyclic Polyethers. 2. Complexes with Organic Acids in 1,2-Dichloroethane

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Abstract: The complexation of *p*-toluenesulfonic, picric, and benzoic acid in 1,2-dichloroethane with the tetraoxa, pentaoxa and hexaoxa "crown" ethers has been investigated conductometrically. Spectrophotometric measurements supplemented conductometric results for the picric acid complexes. It was shown that the affinity of the investigated acids towards complexation with crown ethers increases in the same order as their p*K* values in water. Dicyclohexyl-18-crown-6 (isomer A) has been found to act as the most effective proton binding agent among the investigated crown compounds. The relative ease of ionization of the complexes formed has been discussed in terms of the separation of the ion pair due to proton complexation. The formation and ionization constants of various complexes have been calculated and the constants of formation of free "crownated" protons (oxonium ions) have been estimated.

The ability of macrocyclic polyethers[1] to bind metals[1,2] and various amino compounds[3] has been extensively investigated and several reviews of the subject appeared in recent years.[4-6] It was reported in the first part of this study[7a] that macrocyclic polyethers may also act as powerful proton solvating agents. For instance, it was shown that solutions of hydrobromic acid in chloroform become highly conductive upon addition of a macrocyclic polyether.

Solubilization and ionization of acids in nonpolar low dielectric constant solvents seems to be of considerable interest for acid-base catalysis, electrochemical processes, and various separation techniques such as, e.g., solvent extraction or selective membrane permeation. Nevertheless, besides our original publication,[7a] only a few investigations deal with the proton binding abilities of the macrocyclic polyethers. Izatt et al.[8] reported on a crystalline oxonium ion complex of a monohydrated perchloric acid with isomer A of dicyclohexyl-18-crown-6. Poonia[9] isolated mixed complexes of macrocyclic polyethers with organic acids and alkali metal salts. Cram et al.[10] noted that "crown" compounds are preferentially adsorbed by an ion-exchange resin in its H^+ form. All these investigations have only been indirectly related to the complexation reactions in solution.

We decided, therefore, to undertake a systematic study of the proton binding capabilities of various macrocyclic polyethers. The results of conductometric and spectrophotometric investigation of the complexation of a number of organic acids with "crown" compounds of a varying size and configuration are reported in the present paper.

Experimental Section

2,3,4,5,8,9-Hexahydro-1,4,7,10-tetraoxabenzocyclododecin (Benzo-12-crown-4) (B 12/4); 2,3,5,6,7,9,10-heptahydro-1,4,8,11-tetraoxabenzocyclotridecin (Benzo-13-crown-4) (B 13/4); 6,7,8,15,16,17-hexahydrodibenzo[*b,i*][1,5,8,12]tetraoxacyclotetradecin (Dibenzo-14-crown-4) (DB 14/4); 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin (Benzo-15-crown-5) (B 15/5), and 6,7,8,10,12,18,20,21-octahydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecin (Dibenzo-18-crown-6) (DBC) were prepared following Pedersen.[1] It was found, however, that the reaction yields could in some cases be greatly improved[11] by modifying the original procedures. Thus, LiOH instead of NaOH was used for ring closure of "tetraoxa-crowns". 1,3-Bis(2-hydroxyethoxy)propane for the preparation of B 13/4 was synthesized by reacting at room temperature the monosodium glycolate (formed by NaH in an excess of ethylene glycol) with the 1,3-dibromopropane (Fluka, A.G.). The reaction product was distilled in vacuum (105 °C (0.2 Torr)) and chlorinated by thionyl chloride. B 12/4 and B 13/4 were purified by vacuum distillation (116 °C (0.2 Torr) and 90 °C (5×10^{-2} Torr), respectively). The preparation of DB 14/4 was carried in two steps. To avoid formation of small-membered rings, the first mole of 1,3-dibromopropane was added to a concentrated solution of catechol. The reaction mixture was then diluted and the second mole of 1,3-dibromopropane was added. The final product was purified by recrystallization from methanol. B 15/5 was purified by recrystallization from *n*-heptane. DBC was purified as described elsewhere.[12] 1,4,7,10,13-Pentaoxacyclopentadecane (15/CR/5), PCR Inc., was used without further purification. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18/CR/6), PCR Inc., was purified from traces of water by azeotropic distillation with benzene. Perhydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecin (dicyclohexyl-18-crown-6) (DCC), Aldrich, technical, was first purified on an alumina column (Baker, acid washed), and eluted with hexane. The "crown" compounds in the eluate were detected by shaking chloroform solutions with $KMnO_4$ crystals. The two isomers have been isolated and purified as described by Frensdorff.[13] Thus, obtained cis-syn-cis isomer (DCC/A) has mp 61 °C and cis-anti-cis (DCC/B) has mp 66 °C. *p*-Toluenesulfonic acid (PTS), Merck, G.R., was obtained in anhydrous form by vacuum distillation (140 °C (2 Torr)); picric acid (PA), BDH, A.R., was dried in a vacuum oven (2 h, 60 °C (10 Torr)); benzoic acid, BDH, A.R., was used without further purification. 1,2-Dichloroethane (DCE), Frutasom, CP, was purified on an alumina column, Woelm, neutral. It had $\kappa_{sp} \leq 10^{-9}$ ohm^{-1} cm^{-1}, $D_{25} = 10.36$.

The electronic spectra of the solutions were recorded on a Cary-15 spectrophotometer. Quartz optical cells (0.2-1.0 cm) with Teflon ground-joint stoppers were used in all determinations.

Viscosities of the solutions were checked with an Ubbelohde viscosimeter, and were found to be nearly identical with the viscosity of the pure solvent, $\eta_{25} = 0.8$ cp, in the experimental concentration range.

Hewlett-Packard Model 7620A research gas chromatograph with a "poro pack" type Q33 column was used to check the investigated solutions for the presence of traces of water.

A 1680-A, General Radio automatic capacitance bridge assembly and a conductivity cell with sealed-in platinum electrodes (cell constant 2.30 cm), thermostated in an oil bath at 25.0 ± 0.1 °C were used in conductance measurements. Each value was verified by at least two independent experiments. Typical values of conductivities of PTS solutions are shown in Table I.

Calculations. The ionization and the formation constants of the complexes have been calculated from the measured conductivities by considering the following equilibria:

$$\mathrm{CR} + \mathrm{A}^-,\mathrm{H}^+ \xrightleftharpoons{K_c} \mathrm{A}^-,(\mathrm{HCR})^+ \quad (1)$$

$$\mathrm{A}^-,(\mathrm{HCR})^+ \xrightleftharpoons{K_D} \mathrm{A}^- + (\mathrm{HCR})^+ \quad (2)$$

The conductivities of the analyzed solutions have increased by at least three orders of magnitude upon addition of appropriate "crown" compounds. Accordingly, the contributions due to the two other equilibria

$$\mathrm{A}^-,\mathrm{H}^+ \xrightleftharpoons{K_A} \mathrm{A}^- + \mathrm{H}^+ \text{ and } \mathrm{H}^+ + \mathrm{CR} \xrightleftharpoons{K_f} (\mathrm{HCR})^+$$

Table I. Typical Values of the Specific Conductance at 25 °C of *p*-Toluenesulfonic Acid Solutions in 1,2-Dichloroethane in Presence of Various "Crown" Ethers

"Crown" ether concn, mM	PTS, mM	$\kappa \times 10^6$, ohm^{-1} cm^{-1}
3.29 (15/CR/5)	0.214	0.26 ± 0.02
27.40	1.780	1.66 ± 0.03
1.46 (B 15/5)	0.185	0.31 ± 0.005
12.20	1.540	1.64 ± 0.02
1.75 (DBC)	0.192	0.40 ± 0.02
10.90	1.200	3.46 ± 0.15
1.20 (18/CR/6)	1.200	17.8 ± 0.2
10.00	10.000	95.5 ± 0.3
0.24 (DCC/B)	0.240	5.28 ± 0.02
1.20	1.200	20.72 ± 0.01
0.195 (DCC/A)	0.195	4.95 ± 0.02
10.60	0.578	17.93 ± 0.02

which must be simultaneously maintained in the system, could be neglected. $[A^-] = [(HCR)^+]$ has been denoted as d and $[A^-,H^+]_0$ as H_0.

It follows from eq 1 and 2 that:

$$K_CK_D = d^2f^2/[CR][A^-,H^+] \quad (3)$$

$$H_0 = d + [A^-,H^+] + [A^-,(HCR)^+] \quad (4)$$

where f is the average activity coefficient of the free ions, d, present in solution and the terms in brackets denote the equilibrium concentrations of the crown, the acid, and the complex, respectively.

The experimentally determined conductivity, κ, divided by the concentration of the free ions has been denoted as Λ'. Please note that $\Lambda' = \kappa 10^3/d$, represents the equivalent conductance of the free ions present in solution (cf. discussion on p 250 of ref 7b). Accordingly, for $[CR]_0 \gg H_0$, an algebraic rearrangement of eq 3 and 4 yields:

$$\left(\frac{H_0(\Lambda')^2 \times 10^{-6}}{\kappa^2} - \frac{\Lambda' \times 10^{-3}}{\kappa}\right)\frac{1}{f^2} = \frac{1}{K_D} + \frac{1}{K_CK_D}\frac{1}{[CR]_0} \quad (5)$$

A similar treatment for $[CR]_0 = H_0$ yields:

$$\frac{H_0\Lambda'\,10^{-3}}{f\kappa} - \frac{1}{f} = \frac{1}{\sqrt{K_CK_D}} + \frac{f\kappa}{K_D\Lambda' \times 10^{-3}} \quad (6)$$

Values of f and Λ' have been calculated by computer iteration procedure, analogous to the Fuoss treatment,[14] using the Debye-Huckel and Onsager basic relationships. The latter predicts: $\Lambda' = \Lambda_0 - (\alpha_1\Lambda_0 + \alpha_2)\sqrt{d}$,. Substitutions of d by $\kappa 10^3/\Lambda'$ yield

$$\Lambda' = \Lambda_0 - \beta\kappa^{1/2}10^{3/2}[\Lambda_0 - \beta\kappa^{1/2}10^{3/2}(\Lambda_0 - \beta\kappa^{1/2}10^{3/2}(\ldots(\ldots) \times^{-1/2}\ldots)^{-1/2})^{-1/2}]^{-1/2}$$

where $\beta = \alpha_1\Lambda_0 + \alpha_2$.

Please note that $\Lambda' = \Lambda_0F(\Lambda_0,\kappa)$ and eq 5 becomes identical with the Fuoss equation,[14] $F/\Lambda = 1/\Lambda_0 + (f^2/F)C\Lambda/K_D\Lambda_0^2$, for $K_C[CR]_0 \to \infty$. In such a case the second term on the right side of eq 5 vanishes and $H_0 = C$, $H_0/\kappa 10^3 = 1/\Lambda$, and $\kappa 10^3 = C\Lambda$. Such situation, which corresponds to the total complexation of the acid used, could be realized in the PTS-DCC/A system. In this case, Λ_0, which must be known in order to calculate K_C and K_D from eq 5 or from eq 6, could be experimentally determined. The usual statistical computations[15] of standard deviations were used to estimate the accuracy of the K_C and K_D values derived from the best least-squares lines.

Results and Discussion

The solvation of acids by water molecules has been extensively researched. Numerous detailed crystallographic investigations deal with the subject.[16,17] It was found that only two oxygens are directly involved in the solvation of a proton, though additional water molecules may be hydrogen bonded to the hydrated acid.[16a] The distance between the two oxygens interacting with a proton was found to be significantly shorter than the 2.76-Å characteristic of the normal hydrogen-bonded water molecules,[16,17] namely, a distance of 2.4-2.5 Å was observed.[18] The bonding arrangement about the two oxygens was found to be pyramidal with angles close to tetrahedral. Proton has been found to be located on the line connecting the two oxygens. It is, however, believed[17] that it may occupy a slightly asymmetric position.

On the assumption that bond arrangements and bond distances in the hydrated and in the etherated protons should be similar, one could consider the possibility that small macrocyclic polyethers may be well suited for the complexation of protons. It was pointed out[7a] that oxygens located in the 1,3-positions of the macrocyclic ring may be most effective in this respect (the 1,2-oxygens cannot be aligned in the required fashion). Accordingly the "tetraoxa-crowns" were first tested for their proton-binding ability.

Preliminary experiments conducted with these crowns and with PTS and picric acids gave, however, entirely negative results. Sparsely soluble in 1,2-dichloroethane, PTS could not be solubilized in this solvent upon addition of the B 12/4, B 13/4, or DB 14/4 "crowns", and no change in the optical spectrum or increase in the conductivity could be induced upon their addition to the picric acid solutions.

What is the reason for this apparent lack of interaction between the tetraoxa-crowns and the investigated acids? On the basis of the analogy with the hydration of protons, one may assume that a polyether will act as an effective proton solvating agent when two of its oxygens can be properly aligned at a distance of about 2.5 Å. Such an alignment should be of course achieved without a considerable energy and entropy expenditure. In principle, such alignment of oxygens is possible in the investigated tetraoxa-crowns. However, close examination of the molecular models reveals that it leads to highly strained and crowded conformations of these compounds. Formation of a complex would freeze nearly all segmental motions in the complexed molecule. The interactions of the tetraoxa-crowns with protons seem to be, therefore, prohibited both on enthalpy and entropy grounds.

The situation is drastically changed, however, when somewhat larger polyethers are used. "Crowns" with five or even better with six oxygen atoms seem to act in 1,2-dichloroethane as very effective proton complexing agents.

PTS, which is very sparsely soluble in DCE, is easily solubilized in this solvent upon addition of such "crown" compounds. Thus formed solutions of PTS in DCE are conductive. Typical conductivity values are listed in Table I.

Picric acid solutions in DCE also become conductive, though to a lesser extent, in the presence of the hexaoxa-crown ethers. At the same time a strong bathochromic shift in the spectrum of the picric acid is noted (cf. Figure 1). Smid et al.[20] reported recently on the spectral characteristics of various alkali metal picrates complexed in THF with bis(crown ethers). Comparison of their results with the tracings in Figure 1 shows that the spectra of the complexed picric salts and of the PA-DCC/A complex (λ_{max} 378 nm, ϵ 16 500) are very similar. The former were attributed[20] to the "crown" separated ion pairs or to the free picrate ions. The same must be true for the PA-DCC/A system. In such a case, the nature of the counterion will, of course, be of no importance.

The spectra of the PA-(18/CR/6) mixtures at 5×10^{-3}-5×10^{-2} "crown" concentrations ($\lambda_{max} \sim 350$ nm) resemble those of the uncomplexed picrate salts in THF. Picric acid complexed with the flexible 18/CR/6 may, perhaps, still retain the form of a relatively tight ion pair. The very broad spectrum observed (cf. Figure 1) may be due to the fact that more than one type of ion pairs is present in these solutions.

Analysis of Conductance Data. Conductance measurements, at a constant $[PTS]_0$ and at increasing DCC/A concentrations, show that in the PTS-DCC/A system a plateau in conductivity value is attained at relatively low concentrations of DCC/A (about fourfold excess of DCC/A over PTS seems to be sufficient). A complete conversion of PTS into a complex may be,

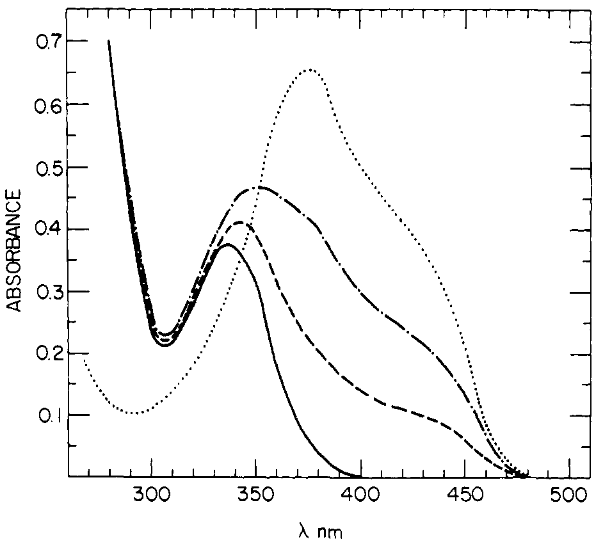

Figure 1. Absorption spectra of 8×10^{-5} M solutions of PA in DCE in the presence of DCC/A and 18/CR/6. Optical cell, 1 cm: (—) no "crown" added; (- - -) 5×10^{-3} M 18/CR/6; (- • - - • -) 5×10^{-2} M 18/CR/6; (• • • • •) 0.2 M DCC/A.

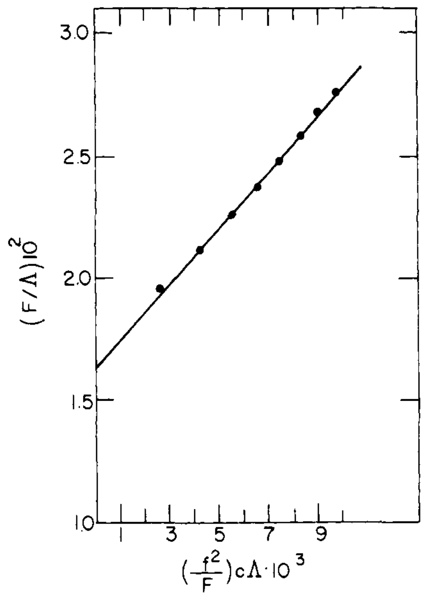

Figure 2. Fuoss plot for PTS in DCE at 25 °C in the presence of a large excess of DCC/A. ($[\mathrm{PTS}]_0$ in the range 0.07-0.7 mM, $[\mathrm{DCC/A}]_0 = 10.6$ mM).

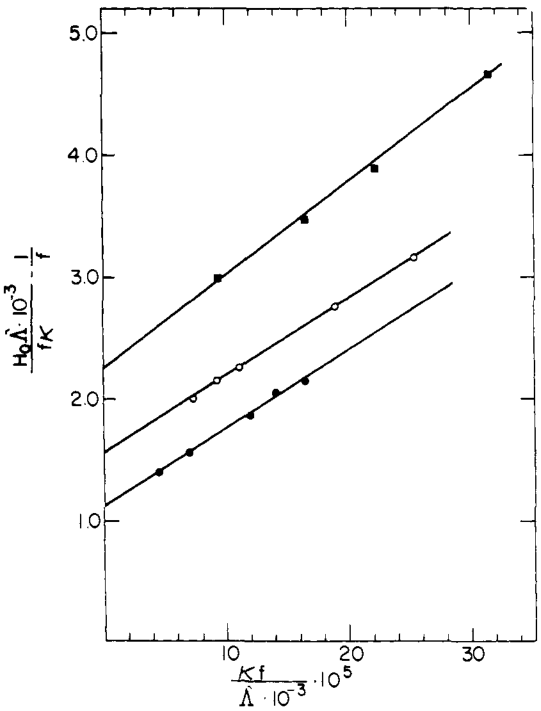

Figure 3. Plots of $(H_0\Lambda' 10^{-3}/f\kappa) - 1/f$ vs. $\kappa f/\Lambda'$ for PTS in DCE at 25 °C for equal PTS and "crown" concentrations (0.1-2 mM): ● DCC/A; ○ DCC/B; ■ 18/CR/6.

therefore, easily achieved in the PTS-DCC/A system. Accordingly, Fuoss treatment[14] could be applied to derive K_D and Λ_0 of this system (cf. Experimental Section, Calculations). Plot of F/Λ vs. $(f^2/F)C\Lambda$ for $[\mathrm{DCC/A}]_0 > 20[\mathrm{PTS}]_0$, is shown in Figure 2. Its slope and intercept yield $K_D = (2.3 \pm 0.2 \times 10^{-4}$ M and $\Lambda_0 = 61.5 \pm 0.5$. The limiting equivalent conductance of the PTS-DCC/A complex was further used in computations based on application of eq 5 and 6 (see Experimental Section). Although the exact values of Λ_0 are probably slightly different for various complexes, the error due to the use of the same Λ_0 in the computations of K_C's and K_D's of all investigated complexes of the hexaoxa-crown ethers does not seem to be large. The inspection of molecular models reveals that the effective cross-sections of the protonated DCC/A, DCC/B, and 18/CR/6 are similar. On the other hand, the dimensions of the PTS and of the PA anions are nearly identical.

All three dimensions of the 15/5 "crown" ethers differ considerably from those of the 18/6 compounds, the effective cross-sections of their complexes with protons must be, therefore, significantly smaller than those of the 18/6 complexes. Accordingly, a value of $\Lambda_0 = 65$ estimated, using the Stokes' relationship, $\Lambda_0^{25} = 0.82|Z|/\eta r$, has been used in the computations.[21]

Reliable values of K_C can be derived only from experiments in which the fraction of the complex is not very large. Hexaoxa-crowns are very effective in complexing PTS. Hence, the condition $[\mathrm{PTS}]_0 = [\mathrm{CR}]_0$ has been imposed on experiments with the PTS-18/6 systems. Thus, eq 6 (see Experimental Section) could be used in the analysis of the experimentally determined conductivities. Resulting plots of $(H_0\Lambda'/f\kappa) - 1/f$ vs. $\kappa f/\Lambda'$ are shown in Figure 3. Reciprocals of their intercepts yield $(K_C K_D)^{1/2}$ and of their slopes K_D values, respectively.

A large excess of a "crown" (in respect to acid) was required to achieve a significant degree of complexation in the PTS-15/5 and in all investigated PA systems. Thus, the condition $[\mathrm{CR}]_0 \gg \mathrm{H}_0$ has been maintained in these systems. Accordingly, eq 5 has to be used in the computations. Resulting plots of $(H_0[\Lambda']^2\, 10^{-3}/(\kappa f)^2 - \Lambda'/\kappa f^2)$ vs. $1/\mathrm{CR}_0$ are shown in Figures 4 and 5. With the possible exception of the 15/CR/5 system, the results conform very well to the predicted linear relationships. Reciprocals of the slopes and of the intercepts of the resulting straight lines yield the $K_C K_D$ and the K_D values, respectively.

Apparently for the 15/CR/5-PTS system, points computed from eq 5 deviate from linearity. This may indicate that the assumption of a 1:1 stoichiometry (which is implicit in derivation of eq 5) represents in this case a crude oversimplification. It is possible that in the high concentration range of this flexible crown ether (which is imposed by its low complexing power) a 2:1 complex (two "crown" molecules per proton) may be also formed in addition to the usual 1:1 complex.

Comparison of the Conductance and of the Optical Absorbance of the PA, DCC/A Solutions. The conductance and the 378-nm absorbance of the 8×10^{-5} M solutions of PA in DCE at increasing DCC/A concentrations (for $[\mathrm{DCC}]_0 \gg [\mathrm{PA}]_0]$ is depicted graphically in Figure 6. The combined spectral and conductivity results provide an alternative route for the cal-

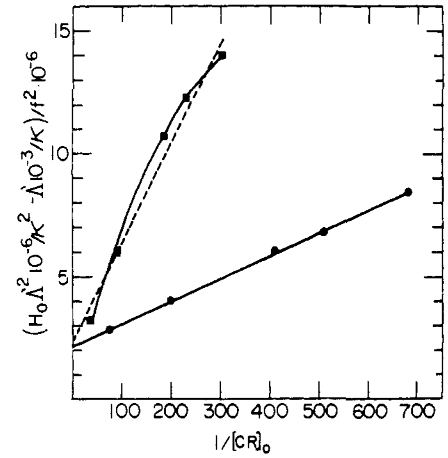

Figure 4. Plots of $(H_0(\Lambda')^2 10^{-6}/\kappa^2) - (\Lambda' 10^{-3}/\kappa)/f^2 \times 10^{-6}$ vs. $1/[\mathrm{CR}]_0$ for PTS in DCE at 25 °C in the presence of an excess of pentaoxa-crown ethers. $[\mathrm{PTS}]_0$ in the range of 0.2-2 mM: ● B 15/5; ■ 15/CR/5.

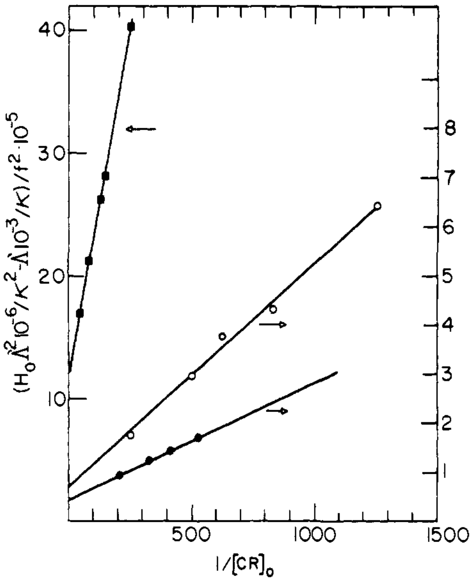

Figure 5. Plots of $(H_0(\Lambda')^2 10^{-6}/\kappa^2) - (\Lambda' 10^{-3}/\kappa)/f^2 \times 10^{-6}$ vs. $1/[\mathrm{CR}]_0$ for PA in DCE at 25 °C in the presence of an excess of hexaoxa-crown ethers. $[\mathrm{PA}]_0$ in the range of 0.1-1.0 mM: ● DCC/A; ○ DCC/B; ■ 18/CR/6.

culation[22] of the K_C and of the K_D values of the PA-DCC/A complex.

A plot of K_C' vs. $\Lambda'/f^2\kappa$ derived from such calculations (see footnote 22) is shown in Figure 7. Its intercept yields the K_C and its slope the K_CK_D value. It is evident from data listed in Table II that thus obtained values and those derived from conductance measurements only are identical within the experimental accuracy.

Inspection of the tabulated data reveals that among the investigated "crown" ethers, the DCC/A "crown" acts as the most effective proton complexing agent. The increase in the efficiency, due to substitution in the macrocyclic ring, may be attributed to the resulting decrease in the flexibility of the macrocyclic ring. Hence, entropy losses due to restriction of segmental motions caused by complexation are minimized.

The low complexing power of the pentaoxa-crowns can be also explained on entropy grounds. In these macrocyclic ethers constraints imposed on segmental movements upon complex formation must be more severe than in the larger hexaoxa-crown ethers. Apparently, for the same reason the tetraoxa-crowns are totally ineffective (cf. preceding section).

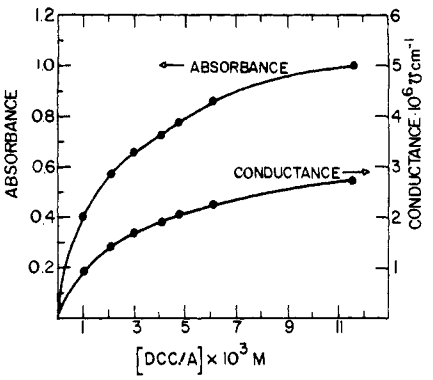

Figure 6. The absorbance and the conductivity of 8×10^{-5} M solutions of PA in DCE at 25 °C at increasing concentrations of DCC/A.

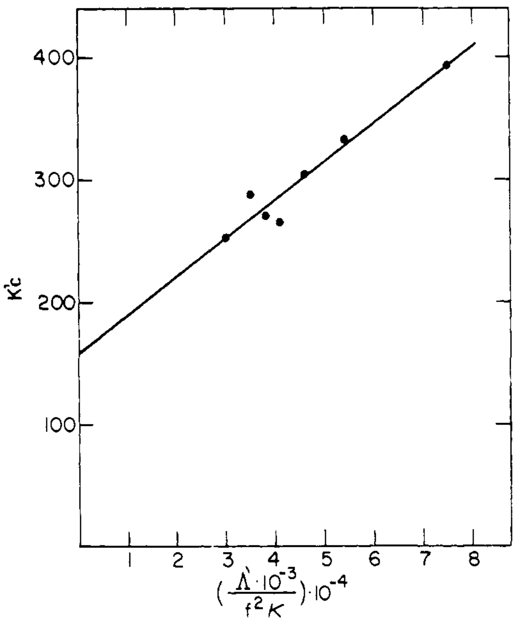

Figure 7. Plots of K_C' vs. $\Lambda'/f^2\kappa$ for 8×10^{-5} M solutions of PA in DCE at 25 °C for concentrations of DCC/A in the range of 1-12 mM.

The high effectiveness of the DCC/A seems to be due to the fact that more conformers, in which two oxygen atoms are aligned in a proper way, are available for this cis-syn-cis isomer[23] than for the DCC/B (a cis-anti-cis isomer[24]) compound.

For PTS and PA the order of their affinities toward complexation with crown ethers is the same as their respective acidities in water. Apparently, the higher the polarizability of the OH group, the more favored is the interaction of its hydrogen with the "crown" polyether. This conclusion is also supported by the results obtained in experiments conducted with benzoic acid, which is a much weaker acid than PA (the pK values of the three acids are −5.4, 0.3, and 4.2, respectively). Namely, the addition of large amounts of the investigated crown ethers to the solutions of benzoic acids in DCE did not induce any significant conductivity in such solutions.

The comparison of the actual values of the ionization constants of the PTS and PA complexes of the two DCC isomers calls for a comment. K_D's of the PTS-DCC complexes are one order of magnitude higher than those of the PA-DCC complexes. The difference is, therefore, much smaller than that of the pK values of the two acids. Why is the effect of DCC more pronounced for PA than for PTS? The reason is easily understood when one recollects that in the case of PA a close approach of the bulky DCC is barred by the two nitro groups

Table II. Formation and Ionic Dissociation Constants at 25 °C of the "Crown" Complexes of the Picric (PA) and *p*-Toluenesulfonic (PTS) Acids in DCE

Acid	DCC/A	DCC/B	18/CR/6	B 15/5	15/5
PTS K_CK_D	0.796	0.416	0.198	1.1×10^{-4}	$\sim 2.4 \times 10^{-5}$
$K_C \times 10^{-2}$, M^{-1}	49.8 ± 4.5	26.2 ± 0.6	15.0 ± 1.0	2.3 ± 0.02	~0.6
$K_D \times 10^5$, M	16.0 ± 0.9 22.9 ± 0.2[a]	15.9 ± 0.5	13.2 ± 0.5	0.047 ± 0.002	~0.04
PA $K_CK_D \times 10^3$	4.195	2.173	0.819		
$K_C \times 10^{-2}$, M^{-1}	1.8 ± 0.05 1.6 ± 0.2[b]	1.4 ± 0.4	0.9 ± 0.09		
$K_D \times 10^5$, M	2.3 ± 0.04 2.0 ± 0.4[b]	1.5 ± 0.4	0.092 ± 0.009		

[a] Derived from Fuoss plot. [b] Derived from the combined spectrophotometric and conductometric results.[22]

adjacent to the OH group. The proton must be pulled out far away from the O^- group to be able to interact with the DCC oxygens. Consequently, a loose ion pair is formed. As may be seen from Figure 1, this is indeed the case.

The OH group in the PTS molecule is easily accessible. Thus, relatively tight ion pairs may be formed with the hexaoxa-crowns and apparently even tighter ones with the pentaoxa compounds (see Table II). Hence, the effects due to the lower strength of the second acid are partially cancelled by the difference in the nature of the ion pairs which are formed by DCC with PTS or with PA. A different situation may exist in the case of the flexible and less bulky 18/CR/6. As indicated by the small bathochromic shift in the spectrum of its complex with PA (see Figure 1) the PA-18/CR/6 complex may, apparently, also exist in the form of a relatively tight ion pair. Hence, the low ionization constant of this system (cf. 4th row in Table II).

Equilibrium Constants of Formation of $(HCR)^+$. The particular acid used to supply protons for the reaction:

$$H^+ + CR \overset{K_f}{\rightleftharpoons} (HCR)^+$$

leading to the formation of the free oxonium ions, should not affect the value of K_f. The intrinsic proton binding affinities of various crown ethers are, therefore, expressed by the K_f's, which can be calculated from the respective K_C, K_D, and K_A values (see Experimental Section). In a system in which the equilibria representing the ionization of the complexed and uncomplexed acid are not complicated by the presence (in each case) of various types of ion pairs, one finds that:

$$K_f = K_D D_C / K_A \qquad (8)$$

where K_A is the dissociation constant of the uncomplexed acid, $HA \rightleftharpoons H^+ + A^-$. Hence, the presently investigated PTS and PA systems should yield, for a given crown ether, a constant ratio of

$$K_A{}^{PTS}/K_A{}^{PA} = (K_CK_D)^{PTS}/(K_CK_D)^{PA} = \text{constant} \qquad (9)$$

Values of Table II for DCC/A and DCC/B yield $K_A{}^{PTS}/K_A{}^{PA}$ = 192.1 and 191.6, respectively. The self-consistency of the results for the two systems is most gratifying. Calculations based on results obtained for the 18/CR/6 system yield, however, a much higher ratio of $K_A{}^{PTS}/K_A{}^{PA}$. This discrepancy indicates that the simplifying assumption underlying derivation of eq 8 (one type of ion pairs defines sufficiently the complexed acid) may not be valid in the PA-18/CR/6 system. In fact, it seems reasonable to expect formation of both tight and loose ion pairs in this case. Such behavior of crown ether complexes has been, indeed, observed and discussed in the literature.[25]

Absolute values of K_f for DCC/A and DCC/B can be calculated from eq 8 if the ionization constant of PA or of PTS in DCE is known. Since the solubility of uncomplexed PTS in DCE is negligible, an effort was made to estimate the ionization of an uncomplexed picric acid in this solvent.

The conductivity of a 0.1 M solution of PA in DCE has been found to be $\sim 7 \times 10^{-8}$ ohm^{-1} cm^{-1}. Thus, using $\Lambda' \sim 70$, one finds $K_A{}^{PA} \sim 10^{-11}$ M. Substitution of this value and of respective K_C and K_D in eq 8 yields values of $K_f{}^{DCC/A} = 4 \times 10^8$ M and of $K_f{}^{DCC/B} = 2 \times 10^8$ M. As pointed out earlier, this difference in complexing ability of the two isomers probably reflects on the difference in the number of conformers with conformations suitable for oxonium ion formation.

A question may be raised at this point if the possibility can be ruled out that hydronium ions and not protons have been actually involved in the investigated complexation reactions. Obviously, the former ions will be favored in the presence of adventitious water. Water was not detected in the investigated solutions by chromatographic measurements (see Experimental Section). However, its traces in the range of 10^{-5} M could still be present.

It seems that such traces could have had only a marginal effect on our results. The conclusion concerning the negligible concentrations of hydronium ions under the experimental conditions is also supported by the observation that the addition of small amounts of water to the investigated solutions strongly affected their conductivity. Namely, an increase in conductivity was noted in the case of the presently described acids. However, an opposite effect has also been recently observed in this laboratory[26] in the case of the trifluoroacetic acid-crown systems.

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(22) The spectral characteristics of free PA ions and their loose ion pairs (PA–DCC/A complex) are assumed to be identical. Accordingly: $I = \epsilon_2(d + b) + \epsilon_1 a$, where a, b, d, ϵ_1, and ϵ_2 denote the uncomplexed acid, the complex (unionized), the free ions, and their extinction coefficients respectively. Hence, $H_0 = a + b + d$, $I_{max} = \epsilon_2 H_0$ and $I_0 = \epsilon_1 H_0$. Let us denote the ratio $(d + b)/a[CR]$ as K_C'. Accordingly: $K_C' = (I - I_0)/(I_{max} - I)[CR]$, $K_C = b/a[CR]$, $K_D = d^2 f^2/b$. It follows that:

$$K_C' = K_C + K_C K_D \Lambda' \, 10^{-3}/f^2 \kappa \tag{7}$$

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Decarboxylations of Azodicarboxylates by Nitrosonium and Nitronium Salts. Decarboxylative Oxidation and Substitution Reactions[1a]

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Abstract: Azodicarboxylates react with nitrosonium salts by two identifiable decarboxylative pathways, one leading to carbon dioxide, nitric oxide, and nitrogen (decarboxylative oxidation) and the other producing carbon dioxide and nitrous oxide (decarboxylative substitution). Association of the nitrosyl cation with the carbonyl oxygen of azodicarboxylate esters is observed in reactions with nitrosonium salts. Subsequent decomposition of the nitrosated ester is dependent on the stability of the alkyl cation generated in the decarboxylation process. The formation of nitrous oxide from nitrosation of potassium azodicarboxylate intimates the involvement of a linear dimer of nitrous oxide. Nitronium salts react with azodicarboxylates to yield dinitrogen tetroxide, nitrogen, and carbon dioxide. In contrast to nitrosative decomposition of azodicarboxylate esters, however, nitrative decomposition is not observably influenced by carbocation stability; these results permit a direct comparison of the electrophilic reactivity of nitrosonium and nitronium salts. The reactivity of azodicarboxylates toward dinitrogen tetroxide and of oxalates with nitrosonium and nitronium salts is also examined.

The decomposition of potassium azodicarboxylate by Bronsted acids[2] has been of considerable interest and synthetic importance due to the formation of diimide as a reactive chemical intermediate.[3] Surprisingly, analogous reactions of potassium azodicarboxylate or its derivatives with Lewis acids other than the proton have not been reported. If Lewis acids are generally capable of effecting decarboxylative substitution their reactions with azodicarboxylates will afford a new and valuable route to azo (dinitrogen) compounds. Reactions of azodicarboxylates with nitrosonium salts are particularly interesting since decarboxylative substitution will result in the formation of **1**, a linear dimer of nitrous oxide.[4] Decomposition of **1** can occur by two pathways, one leading to $2N_2O$ and one yielding $N_2 + 2NO$. Similar reactions with nitronium salts are expected to result in the formation of dinitrodiazene (**2**), which is predicted to decompose to nitrogen and dinitrogen tetroxide. However, since nitronium and nitrosonium salts are powerful oxidants as well as strong Lewis acids, electron transfer reactions of azodicarboxylates with these ions must also be considered.

$$2A^+ + {}^-O_2C{-}N{=}N{-}CO_2{}^- \rightarrow A{-}N{=}N{-}A + 2CO_2 \tag{1}$$

$$\underset{\mathbf{1}}{O{=}N{-}N{=}N{-}N{=}O} \qquad \underset{\mathbf{2}}{O_2N{-}N{=}N{-}NO_2}$$

Results and Discussion

Reactions of Azodicarboxylates with Nitrosonium Salts. Azodicarboxylate compounds react rapidly with nitrosonium salts by divergent reaction pathways that reflect the structural nature of the azodicarboxylate derivative. Slow addition of potassium azodicarboxylate to 2 molar equiv of $NO^+BF_4^-$ in acetonitrile at room temperature under strictly anhydrous conditions[5] produces an immediate and rapid evolution of nearly equal amounts of nitrous oxide and carbon dioxide.

$$2NO^+ + {}^-O_2C{-}N{=}N{-}CO_2{}^- \rightarrow 2CO_2 + 2N_2O \tag{2}$$

Nitric oxide and nitrogen are formed in a molar ratio of 2:1 as minor products in this reaction (<15% of the total nitrogen containing gaseous products). When allowances are made on the relative yield of carbon dioxide for the formation of $2NO + N_2 + 2CO_2$, the molar ratio of carbon dioxide to nitrous oxide is 1.0. The stoichiometry of the reaction of nitrosonium tetrafluoroborate with potassium azodicarboxylate, together with the observation of both nitrous oxide and carbon dioxide, suggests the operation of the substitutive decarboxylation pathway for the production of nitrous oxide (Scheme I). A similar scheme may explain the formation of diimide in the protonic decarboxylation of potassium azodicarboxylate.[6]

In Scheme I nitrosation of the azodicarboxylate dianion is described as occurring at oxygen. Subsequent decarboxylative