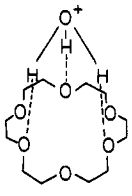
and other solid hydronium ion complexes of 18-crown-6 suggest that the former may involve nitric acid hydrate species rather than hydronium ions. Most probably the two nitric acid monohydrate molecules sandwich a molecule of 18-crown-6. Although an X-ray crystal structure would provide the essential structural information for further clarification, our attempts to grow suitable crystals of this complex have been unsuccessful.

Variation of the Polyether. So that requirements of the polyether component for the formation of solid hydronium ion-polyether complexes could be probed, three unsubstituted crown ethers and several glymes were examined by using concentrated aqueous HPF_6 as the acid component.

As was described previously, the complex formed from 18-crown-6 is a nonhygroscopic, sharp-melting solid with a stoichiometry of $(H_3O^+)(\mathbf{2})(PF_6^-)$. From 15-crown-5, a hygroscopic solid with mp 88–91 °C was isolated. However, integration of the ^1H NMR spectrum for this solid and the results of elemental analysis were both inconsistent with either a uniform 1:1 or 2:1 (two crown ether molecules and one hydronium ion) complex. From 12-crown-4, **3**, a nonhygroscopic complex with mp 98–99 °C and a stoichiometry of $(H_3O^+)(\mathbf{3})_2(PF_6^-)$, was obtained (table). For this complex, the ^1H NMR absorption of the crown ether protons shifts downfield by 0.08 ppm from that of **3**, and the absorption for the hydronium ion protons appears at 9–12 ppm[10] with the exact integration for a 2:1 complex. The IR spectrum of this complex in Nujol exhibits broad absorption in the region of 3600–1600 cm^{-1} and C-O-C stretching vibrations at 1140, 1070, and 1040 cm^{-1} (compared with 1120 and 1100 cm^{-1} for **3**).

Thus, the stoichiometry of hydronium ion-crown ether complexes is found to be highly dependent upon the size of the crown ether. For 18-crown-6, the geometry allows the pyramidal hydronium ion to hydrogen bond with three alternate oxygens of the crown ether and thereby form a stable 1:1 complex, **4**. Similar arrangements have been proposed for the complexation of ammonium and monoalkylammonium ions by this crown ether.[18] On the other hand, it seems most reasonable that the 2:1 complex with 12-crown-4 exists as a sandwich complex of the cation between two molecules of **3** similar to those reported for $(Na^+)(\mathbf{3})_2(Cl^-)\cdot 5H_2O$,[19] $(Na^+)(\mathbf{3})_2(OH^-)\cdot 8H_2O$,[20] and $(Mn^{2+})(\mathbf{3})_2(Br_3^-)_2$.[21] Such an arrangement would allow the hydronium ion to hydrogen bond with two alternate oxygens of one crown ether molecule and one oxygen of the second molecule of **3**, as is illustrated in **5**. The geometry for 15-crown-5 is intermediate between that for 18-crown-6 and 12-crown-4. Therefore, the formation of an ill-defined hydronium ion-crown ether complex with neither 1:1 nor 2:1 stoichiometry is not unreasonable.



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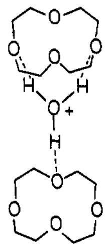

5

An attempt to prepare solid hydronium ion-polyether complexes from acyclic polyethers (glymes) met with limited success. By use of the series of glymes from diglyme through heptaglyme, concentrated aqueous HPF_6 as the acid component, and ^1H NMR to determine the stoichiometry, it was found that only triglyme, tetraglyme, and pentaglyme formed well-defined complexes. Of these 1:1 complexes, only that obtained from tetraglyme was a solid (mp 54–57 °C, 52% yield), whereas those formed by triglyme and pentaglyme were oils. Since both tetraglyme and 15-crown-5 contain five ether oxygen atoms, the formation of a complex with definite stoichiometry only from the former suggests that the greater flexibility of the acyclic polyether allows for better complexation with the hydronium ion.

Experimental Section

^1H NMR spectra were recorded in $CDCl_3$ by using a Varian 360 spectrometer and tetramethylsilane as the internal standard. Infrared spectra were measured with a Beckman Acculab 8 spectrophotometer. Ion chromatography was conducted on a Dionex 16 ion chromatograph. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

Materials. 18-Crown-6, 15-crown-5, 12-crown-4, tetraglyme, triglyme, and diglyme were obtained from Aldrich Chemical Co. and were used directly. Heptaglyme, hexaglyme, and pentaglyme (all acquired from Parish Chemical), dichloromethane (MC & B Omnisolve), HPF_6 (65%, Alfa), HBF_4 (37–40%, Spectrum Chemical), $HClO_4$ (70%, Baker), HI (47%, MC & B), and HBr (48%, MC & B) were used as received.

Procedure. To 1.1 mmol of the crown ether in 4 mL of CH_2Cl_2 in a Pyrex or polyethylene test tube is added 1.5–2.2 mmol[22] of the concentrated aqueous acid. The contents of the test tube are shaken with a vortex mixer for 2 min, and the organic layer is separated and dried with anhydrous magnesium sulfate. The volume of the CH_2Cl_2 solution is reduced to 2 mL in vacuo at room temperature. Addition of anhydrous Et_2O (5 mL) precipitates[23] the complex, which is filtered, washed with anhydrous Et_2O (5 mL), and air-dried.

Registry No. (H_3O^+)(18-crown-6)(PF_6^-), 82280-97-5; (H_3O^+)(18-crown-6)(ClO_4^-), 82280-98-6; (H_3O^+)(18-crown-6)(BF_4^-), 82024-63-3; (H_3O^+)(18-crown-6)(I^-), 82280-99-7; (H_3O^+)(18-crown-6)(Br_3^-), 82281-01-4; $(HNO_3{\cdot}H_2O)_2$(18-crown-6), 82281-02-5; (H_3O^+)(12-crown-4)$_2(PF_6^-)$, 82281-03-6.

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(19) van Remoortere, F. P.; Boer, F. P. *Inorg. Chem.* **1974**, *13*, 2071–2076.

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(22) When the crown ether is 12-crown-4, 3.3 mol of the concentrated acid is used.

(23) If precipitation of the complex is slow, it may be hastened by partial removal of the solvents in vacuo with no external heating.

Acyl Hypobromite: An Intermediate in the Alcohol-Silver Salt-Bromine Reaction

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The reaction of alcohols with bromine and silver salts has been the subject of many papers[2] with particular interest in the role of the solvent,[3] the reaction conditions,[4]

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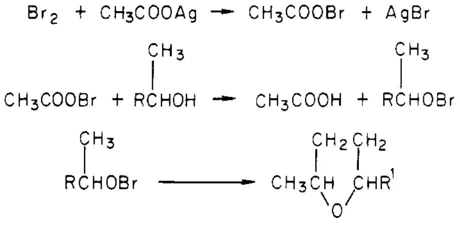
Scheme I



$$Br_2 + CH_3COOAg \rightarrow CH_3COOBr + AgBr$$

$$CH_3COOBr + RCH(CH_3)OH \rightarrow CH_3COOH + RCH(CH_3)OBr$$

$R = CH_3(CH_2)_2$, $R^1 = H$
$R = CH_3(CH_2)_3$, $R^1 = CH_3$
$R = CH_3(CH_2)_5$, $R = CH_2CH_2CH_3$

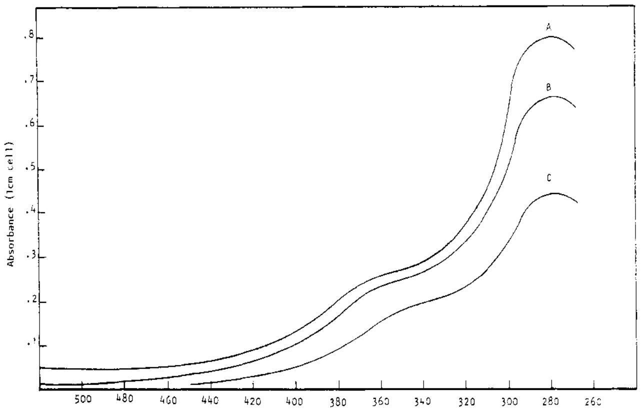


Figure 1. Reaction of 2-hexanol with bromine and silver acetate in the presence of sodium carbonate in carbon tetrachloride at 25 °C: A, 0.2 h; B, 2.9 h; C, 10.9 h.

and the particular kind of silver salt.[5] We have previously reported[5] that the bromine oxidation of alcohols in the presence of silver acetate leads preferentially to tetrahydrofurans as products as compared to silver trifluoroacetate, which leads preferentially to ketones, with nonsilver carboxylates leading to a mixture of products.

A variety of explanations have been offered for this difference,[2] related primarily to the mechanism of the alkyl hypobromite conversion to tetrahydrofurans. We now report that as a result of our attempts to develop a reasonable procedure to follow the kinetics of this heterogeneous reaction, we have identified an additional intermediate in the case of silver carboxylate salts.

Our preliminary studies indicate that the difference in final product is a function of the rate at which this first intermediate can form. By a monitoring of the reaction over time by ultraviolet spectroscopy, the sequence of the reaction can be followed in a way that is transparent to titrimetric studies.

In a typical reaction of an alcohol with silver carboxylate and bromine in carbon tetrachloride, spectroscopic monitoring of the reaction mixture over time indicates three areas of ultraviolet absorption. Free bromine is observed at 415 nm, with the characteristic absorption maxima at 320 nm due to acyl hypobromite from the silver salt[6] and the characteristic absorption maxima at 280 nm due to the alkyl hypobromite.[6]

Separate studies also indicate that the acyl hypobromite exchanges bromine with the alcohol to form the alkyl hypobromite. It is the alkyl hypobromite that then goes on to form the tetrahydrofuran product (Scheme I).

If a silver acetate is used, absorption due to bromine is absent almost immediately, with a fast development of the

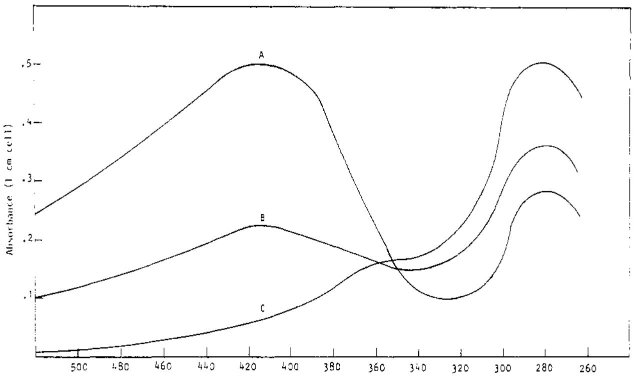


Figure 2. Reaction of 2-hexanol with bromine and silver trifluoroacetate in the presence of sodium carbonate in carbon tetrachloride at 25 °C: A, 0.2 h; B, 1.4 h; C, 3.5 h.

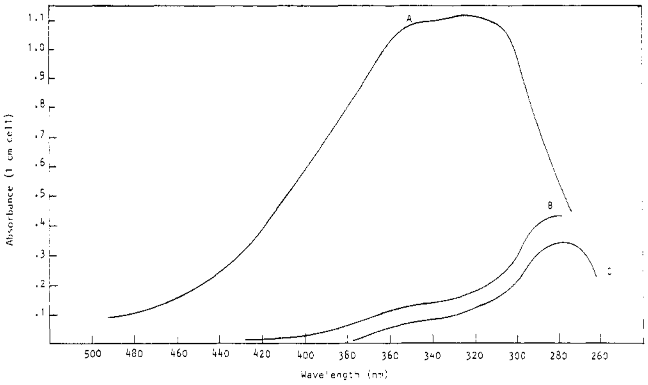


Figure 3. Reaction of bromine with silver acetate in the presence of sodium carbonate in carbon tetrachloride at 25 °C with 2-hexanol added after 0.5 h: A, 0.2 h; B, 0.6 h; C, 9.6 h.

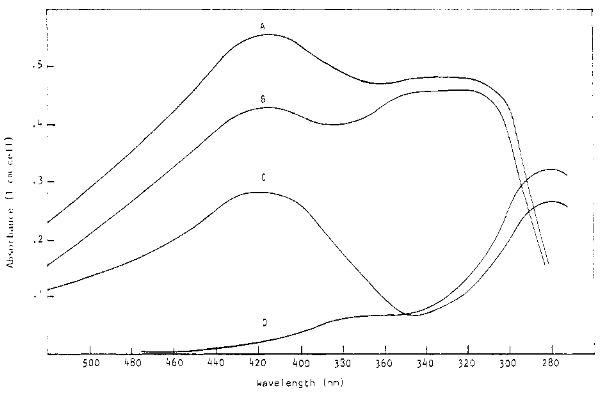


Figure 4. Reaction of bromine with silver trifluoroacetate in the presence of sodium carbonate in carbon tetrachloride at 25 °C with 2-hexanol added after 1.2 h: A, 0.2 h; B, 0.7 h; C, 1.3 h; D, 3.7 h.

alkyl hypobromite of the alcohol (Figure 1).

By contrast, if silver trifluoroacetate is used, the disappearance of bromine is slow. Several hours are required to reach a maximum concentration of alkyl hypobromite. The reaction with 2-hexanol illustrated in Figure 2 is typical.

Studies carried out in the absence of alcohol indicate that with silver acetate, acetyl hypobromite forms immediately. When alcohol is added to the reaction mixture, the acetyl hypobromite undergoes a facile exchange to form the alkyl hypobromite (Figure 3). The alkyl hypobromite then goes on to form product.

If silver trifluoroacetate is reacted with bromine in the absence of alcohol, about 5 h is required to reach a maximum concentration of acyl hypobromite as monitored at

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(6) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

320 nm (Figure 4). Addition of alcohol converts the acyl hypobromite to the alkyl hypobromite immediately. Once the alkyl hypobromite has formed, the rate of formation of product is comparable to that observed in the silver acetate reaction.

In the absence of silver salts under the reaction conditions, the reaction of bromine with the alcohol is slow and no alkyl hypobromite is observed in the ultraviolet. The product formed is the ketone.

We therefore suggest that the difference in product observed in the alcohol–bromine–silver salt reaction between silver acetate and silver trifluoroacetate is a result of two competitive reactions rather than two products from a single reaction as reported previously.[2]

With silver acetate, the tetrahydrofuran product predominates, because of the facile formation of the acetyl hypobromite. Whereas with silver trifluoroacetate, which reacts slowly with bromine, the competitive reaction, to form the ketone via direct reaction of the alcohol with free bromine, can take place.

Experimental Section

All spectrophotometric measurements were made on a Varian Series 634 spectrophotometer.

Starting Materials. Alcohols were commercial samples that gas chromatographic analysis indicated were better than 99% pure. They were used without further purification. The silver salts and bromine were also commercial samples and used without further purification.

Carbon tetrachloride (analytical reagent) was distilled with the fraction boiling 76–77 °C collected. The distillate was dried over anhydrous magnesium sulfate for at least 1 day and filtered immediately before use.

Reaction Procedure. The reactions were carried out in a three-neck flask (1000 mL) fitted with a Tru-bore stirrer.

The flask was wrapped in aluminum foil and placed in a constant-temperature bath at 25 °C. Alcohol and bromine solutions were prepared in separate volumetric flasks and stored in the constant-temperature bath until mixing.

Anhydrous sodium carbonate was added to the reaction flask (0.50 g/100 mL of reaction mixture) as well as the silver salts. After the addition of solids, the alcohol solution was added and the stirrer started. The bromine solution was then added.

Samples were taken from time to time with volumetric pipettes. The samples were placed in a quartz cuvette (1 cm), and the absorbance was measured immediately against a carbon tetrachloride blank scanning from 500 to 265 nm. In all cases, the stirrer was stopped long enough so that samples taken for spectrophotometric analysis did not contain suspended solids.

Kinetics and Mechanism of the Conjugate Hydrocyanation of α,β-Unsaturated Ketones by the Potassium Cyanide–Ammonium Chloride System

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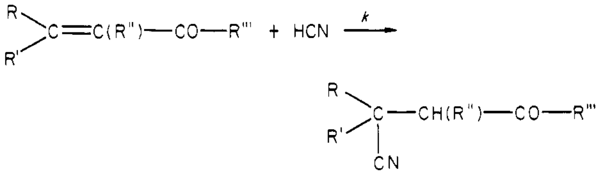
In spite of their huge synthetic importance, nucleophilic additions to electrophilic double bonds were the subject of but a few kinetic studies. Thus, except for an early kinetic work,[1] the hydrogen cyanide addition to α,β-unsaturated ketones has been examined from an almost exclusively stereochemical point of view.[2,3]

We recently described[4] a simple procedure for measuring the apparent rate constant of the potassium cyanide–ammonium chloride reaction with enones in dimethylformamide–water mixtures (eq 1). This method was then



$$\mathrm{RR'C{=}C(R''){-}CO{-}R''' + HCN \xrightarrow{k} RR'C(CN){-}CH(R''){-}CO{-}R'''} \tag{1}$$

applied to the elucidation of stereochemical problems.[4] Although the gross mechanistic features of conjugate hydrocyanation have been known for a long time,[5] it is the purpose of the present work to bring novel information concerning some physicochemical parameters related to the transition state location.

Results and Discussion

The CN^-–NH_4^+ System. Prior to the reactions involving the enone molecule, there is a fast equilibrated reaction (eq 2) between cyanide and ammonium ions. In

$$CN^- + NH_4^+ \rightleftarrows HCN + NH_3 \tag{2}$$

the DMF–water mixture (9:1, v/v) this equilibrium (2) is shifted far to the right. It was indeed reported that the pK_a's of NH_4^+ and HCN, which are very similar in water, are respectively 10.5[6a] and 12.9[6b] in an aprotic medium (Me_2SO). Under these conditions the experimental data show that the cyanide concentration remains constant during the first 50% of the hydrocyanation reaction (1): CN^- acts as a catalyst and HCN is consumed.

This assumption explains the pseudo-first-order rate constant in the rate law

$$\frac{d[\text{enone}]}{dt} = -\frac{k_{ap}}{1 + K_{ap}}[\text{enone}] \tag{3}$$

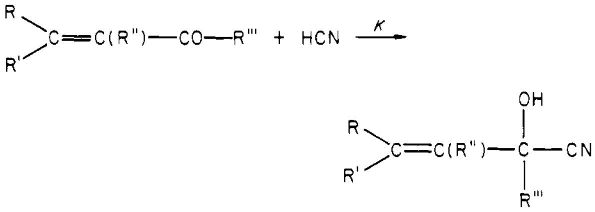
with

$$k_{ap} = k[CN^-] \tag{4}$$

and

$$K_{ap} = K[HCN] \tag{5}$$

K being the equilibrium constant for the formation of the cyanohydrin (eq 6). It should be emphasized that in eq



$$\mathrm{RR'C{=}C(R''){-}CO{-}R''' + HCN \xrightarrow{K} RR'C{=}C(R''){-}C(OH)(R'''){-}CN} \tag{6}$$

3 the $1 + K_{ap}$ term remains practically constant, thus allowing a simple integration of this equation:

$$\ln\,[\text{enone}] = -\frac{k_{ap}}{1 + K_{ap}}t + \ln\,[\text{enone}]_0 \tag{7}$$

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[1] Jones, W. J. *J. Chem. Soc.* **1914**, *105*, 1547.

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