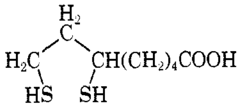
this radical

$$RSS(H)R \rightleftarrows RSSR^- + H^+ \qquad (11)$$

is 5.85 ± 0.1. This acid–base effect is also seen in the second-order decay of protonation of $RSSR^-$, $k_{-11} = 5.5 \times 10^{10}\ M^{-1}\ sec^{-1}$, and is nearly diffusion controlled, as discussed in a previous section, because of the absence of amino groups.

The second-order decay of $RSSR^-$ requires that the bimolecular disappearance of the radical be competitive with its first-order intramolecular decay. Thus, under the conditions of these experiments, where $[RSSR^-] \sim 3 \times 10^{-5}\ M$ and $2k = 1.4 \times 10^8\ M^{-1}\ sec^{-1}$ for the decay of the radical, any first-order component for the disappearance of this radical must have a k less than $\sim 3 \times 10^3\ sec^{-1}$. Because of the close proximity of the sulfur atoms in this cyclic disulfide, the fragments produced upon S–S bond scission cannot diffuse away into the bulk of the solution, and thus intramolecular recombination predominates. The second-order decay of the $RSSR^-$ (and $R\dot{S}SHR$) probably leads to disproportionation, with the formation of the known[18] product dihydrolipoic acid.



The effect of pH on the decay rates of $RSSR^-$ and $R\dot{S}S(H)R$ of lipoic acid, Figure 5, may lie in the differences in their electronic structures: the $RSSR^-$ radical with its large, diffuse, electron density delocalized within the disulfide orbital system, and the sulfenium $R\dot{S}S(H)R$ radical in which the H atom is localized on one sulfur atom and the unpaired electron on the other.

Conclusion

The above results show that all the disulfide linkages have a high reactivity toward solvated electrons, and that the reaction rate constants are dependent upon the acid–base properties of the disulfide compounds. The decay rates of the disulfide radical anions $RSSR^-$ are markedly dependent upon pH. In the neutral to alkaline range, the first-order decay is dependent on the dissociation constants of the amino groups when present in a α position to the –S–S– group. In slightly acidic solutions, the $RSSR^-$ radicals decay by reaction with H^+ to form the corresponding thiyl radicals $RS\cdot$ (presumably *via* the sulfenium radical as intermediate). The kinetics of protonation range from 6.0×10^8 to $7.0 \times 10^{10}\ M^{-1}\ sec^{-1}$ for cystine dimethyl ester to glutathione disulfide, respectively. The reaction of H atoms with disulfide is shown to produce thiyl radicals.

Protonation of Macrocyclic Polyethers. Complexes with Hydrogen Bromide and Hydrogen Tribromide in Chloroform

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Contribution from the Weizmann Institute of Science,
Rehovot, Israel. *Received March 7, 1972*

Abstract: Interaction of polydentate ethers with hydrogen bromide in chloroform solutions has been investigated conductometrically and spectrophotometrically. Complexation of molecular bromine with bromide ions served as a convenient probe for spectroscopic exploration of investigated systems. Polydentate ethers act as efficient ionizing agents, while hydrogen bonding is predominant in the case of monofunctional and certain bifunctional ethers. The macrocyclic polyether dicyclohexyl-18-crown-6 (DCC) was shown to act as an especially powerful proton solvating agent, its very high complexing power being apparently due to a combination of a relatively high basicity with the low entropy of complexation. At 25° the equilibrium constant, K_p, of the reaction DCC + HBr $\rightleftarrows$ $DCCH^+Br^-$ was found to be about $10^6\ M^{-1}$. For the linear polydentate glyme-2 and glyme-3, $K_p = 0.17$ and $0.20\ M^{-1}$ respectively, while for the aromatic macrocyclic polyethers DBC and Br–DBC, the values are 210 and $20\ M^{-1}$. Pertinent values of the entropies and of the enthalpies of complexation have also been determined for glyme-2 and for Br-DBC. In the case of THF and of glyme-1, the equilibrium constants, $K_1^{25°}$, of the hydrogen bonding interaction $R_2O + HBr \rightleftarrows R_2O\cdots HBr$, were found to be 50 and $13\ M^{-1}$, respectively, while the equilibrium constants of the formation of the ionic complexes were found to be about $0.6 \times 10^{-4}\ M^{-1}$. Study of the complexation reaction $Br_2 + DCCH^+,Br^- \rightleftarrows DCCH^+,Br_3^-$ in chloroform yields $K_5^{25°} = 3.7 \times 10^4\ M^{-1}$, $\Delta H_3 = -8.2$ kcal, and $\Delta S_3 = -6.6$ eu.

The tendency of ethers to form charge-transfer complexes with halogens[1,2] and their ability to form oxonium ions with halogen acids[3,4] and to bind hydrogen halides by strong dipole–dipole interactions,[5,6] as well as to act as effective solvating agents for cations,[7,8] are well established.[9]

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(1) O. Hassel, *Science*, 170, 497 (1970).

(2) M. Tamres and M. Brandon, *J. Amer. Chem. Soc.*, **82**, 2134 (1960).

(3) E. Wiberg, M. Schmidt, and A. G. Galinos, *Angew. Chem.*, **66**, 443 (1954).

(4) F. Klages, H. Meuresch, and W. Steppich, *Justus Liebigs Ann. Chem.*, **592**, 81 (1955).

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(6) G. L. Vidale and R. C. Taylor, *J. Amer. Chem. Soc.*, **78**, 294 (1956).

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(8) H. D. Zook and T. J. Russo, *J. Amer. Chem. Soc.*, **82**, 1258 (1960).

(9) S. Searles, Jr., and M. Tamres, "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967.

The macrocyclic polyethers, a class of compounds recently synthesized by Pedersen,[10] were shown to bind cations much more powerfully than monofunctional and linear polyfunctional ethers of similar basicity.[11-14] A geometric fit between the size of the cation and the dimensions of the "cavity" in the macrocyclic molecule was shown to be, to a large extent, responsible for the stability of such complexes.

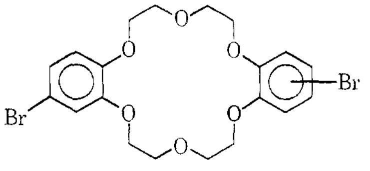
The present study deals with the complexation of hydrogen bromide and of hydrogen tribromide in chloroform solutions with macrocyclic "crown" polyethers. Respective results are compared with those obtained for the complexation with linear polyethers, dioxane and tetrahydrofuran.

The stoichiometry and the equilibrium constants of formation of the hydrogen tribromide complexes were spectrophotometrically determined. The expected enhancement of the ionic dissociation of such complexes was conductometrically confirmed. A profound effect of the polyethers on electrophilic bromine addition reactions was also noted. A detailed study of the influence of polyethers on the addition of bromine to stilbene in the presence of hydrogen bromide is reported elsewhere.[15]

Experimental Section

Dicyclohexyl-18-crown-6 (DCC), pure, E. I. du Pont de Nemours and Co., was used without further purification.

Dibenzo-18-crown-6 (DBC) was prepared according to Pedersen[10] and purified as described elsewhere.[14]



Br -DBC

4,4′-Dibromodibenzo-18-crown-6 (Br-DBC) was synthesized from DBC. Bromine (14 g) was added to a chloroform solution of DBC (15 g in 250 ml) and the reaction mixture was refluxed for about 2 hr; 30 min after the evolution of HBr had ceased, the solution was cooled and the excess of bromine was removed by washing with aqueous ammonium bisulfite. The solvent was evaporated under vacuum, and the product was purified by recrystallization from methyl Cellosolve. Its structure and purity were checked by mass spectroscopy and by pmr. The product contained some monobromo derivative (~10%) and tribromo derivative (~7%); the bulk of the material (~83%) was, however, the 4,4′-dibromo derivative (pmr in $CDCl_3$: singlet of H(3) at δ 6.99 ppm, AB pattern of H(5,6) centered at δ 6.87 ppm, and a broad doublet of etheric methylenes at δ 4.08 ppm).

Triethylene glycol dimethyl ether (glyme-3), Fluka, Purum, was kept over sodium-potassium alloy for 24 hr and distilled at 93° at 4 mm.

Tetrahydrofuran (THF), dioxane, ethylene glycol diethyl ether (glyme-1), and diethylene glycol dimethyl ether (glyme-2), Fluka, Puriss reagents, were refluxed and distilled over sodium or potassium metal and stored under argon.

Chloroform, Frutarom, analytical grade, was washed with water (6 × 500 ml for 1 l. of chloroform), dried over calcium chloride, and distilled over Drierite in an argon atmosphere. Its specific conductance was less than 0.1×10^9 ohm^{-1} cm^{-1}. The above procedure is required in order to remove ethanol which is usually added to chloroform as a stabilizer. The presence of ethanol in chloroform vitiates the results as it competes with ethers for hydrogen bromide and is reactive toward bromine. Freshly distilled chloroform, kept in the dark under argon, was used in all experiments.

Bromine, BDH, Analar, was used without further purification. Its solutions in chloroform were stable for a least 1 day, if kept in the dark.

Hydrogen bromide, Matheson, 99.8% purity, was used; its solutions were prepared by passing the gas through chloroform and drying over Drierite. (Traces of water cause a phase separation with most of HBr in the aqueous phase.)

Methanol, Frutarom, analytical grade, was fractionated and a middle fraction with specific conductivity 0.16×10^{-6} ohm^{-1} cm^{-1} was collected.

All solutions were kept in the dark and used on the day of preparation.

Absorption spectra were recorded on a Cary-15 spectrophotometer. Quartz cells (0.1–5.0 cm) with Teflon ground joint stoppers were used in all determinations.

A constant temperature of ±0.1° was maintained by circulating water from a thermostated bath through a double walled insert equipped with quartz windows. The temperature inside the cell compartment was monitored with a copper-constantan thermocouple.

A 1680-A, General-Radio, automatic capacitance bridge assembly was used in all conductivity measurements. Fisher Catalog No. 9-367 conductivity cell (cell constant 0.65 cm) was thermostated in a paraffin oil bath at 25.0 ± 0.1°.

Analytic Procedures. Bromine concentrations in stock solutions were iodometrically determined with 0.1 and 0.01 *N* sodium thiosulfate solutions. In the presence of "crown" polyethers, magnesium salts, *instead of sodium salts, were used for titrations, as the* latter form stable complexes with the crown ethers, which interfere with titrations.

Hydrogen bromide concentrations in stock solutions were determined iodometrically by the iodide-iodate method. Concentrations of diluted solutions were checked conductometrically or spectrophotometrically: 10^{-5}–10^{-4} solutions of HBr in chloroform were diluted in 1:1 ratio with methanol, and the conductivity of the solutions was measured. Under such conditions, the dissociation of the acid is complete. Its concentration was read from the Λ *vs.* $\sqrt{c}$ calibration curve. The limiting equivalent conductance (Λ_0^{25}) of HBr in the 1:1 chloroform-methanol mixed solvent is 108.

After each spectroscopic experiment, the concentration of HBr was checked by adding an excess of bromine and DCC required to attain its total complexation. The resultant absorbance at 273 mμ (ϵ 48,200) of the tribromide ion yields the overall concentration of HBr.

Results and Discussion

Chloroform solutions of hydrogen bromide or of bromine and hydrogen bromide mixtures are virtually nonconductive. However, a sharp increase in the conductance of the solutions occurs upon addition of a minute amount of a cyclic polyether. The effect of the monofunctional tetrahydrofuran is much less pronounced (see Table I).

Table I. Conductivity of 10^{-3} *M* Hydrogen Bromide in the Presence of Ethers and Bromine in Chloroform Solutions at 25°

Ether concn, m*M*	Br_2, m*M*	$\kappa \times 10^9$, ohm^{-1} cm^{-1}
None	None	0.6
150 (THF)	None	7.8
13 (DCC)	None	1580
None	2.0	1.3
150 (THF)	2.0	63.0
13 (DCC)	2.0	1320

The electronic absorption spectra of the solutions are shown in Figure 1. Their inspection reveals that in the absence of an ether the spectrum of bromine is virtually unaffected by the addition of hydrogen bromide. However, after addition of an ether, the absorption

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[10] C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

[11] (a) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971); (b) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

[12] H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971).

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[14] E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *ibid.*, **93**, 7133 (1971).

[15] E. Shchori and J. Jagur-Grodzinski, *Isr. J. Chem.*, in press.

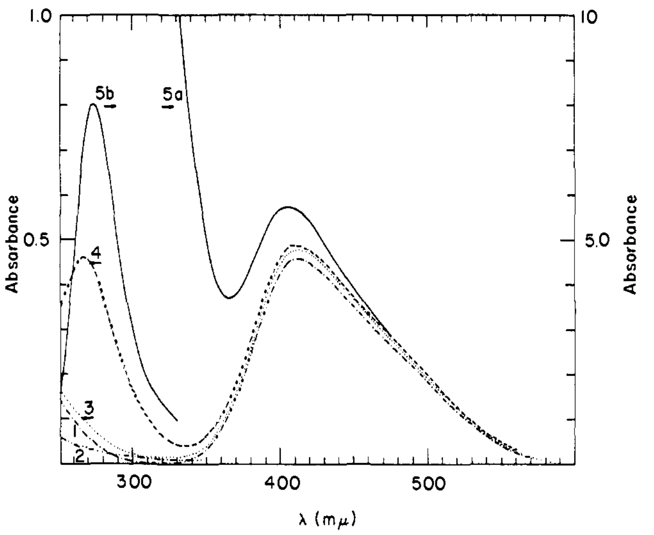

Figure 1. The electronic absorption spectra of bromine and its complexes in chloroform. (1) – · – · –, $[Br_2] = 2.225 \times 10^{-3}\ M$; (2) – · · – · ·, $[HBr] = 1.51 \times 10^{-3}\ M$; (3) · · · · ·, $[Br_2] = 2.225 \times 10^{-3}\ M$, $[HBr] = 1.51 \times 10^{-3}\ M$; (4) – – – – – –, $[Br_2] = 2.225 \times 10^{-3}\ M$, $[HBr] = 1.51 \times 10^{-3}\ M$, $[THF] = 0.194\ M$; (5) ———, $[Br_2] = 2.225 \times 10^{-3}\ M$, $[HBr] = 1.51 \times 10^{-3}\ M$, $[DCC] = 0.163 \times 10^{-3}\ M$. (a) Left-hand coordinate, (b) right-hand coordinate.

band of the Br_3^- complex, at 270–273 mμ, appears. A similar effect is also observed on addition of an alcohol to the chloroform solution of HBr and Br_2. Apparently, as a result of the interaction with ether, the covalently bonded hydrogen bromide may be converted into an ion pair, which may further complex with a bromine molecule.

$$HBr + n(\text{ether}) + Br_2 \overset{K_{ov}}{\rightleftharpoons} H^+(\text{ether})_n,Br_3^- \qquad (1)$$

$$H^+(\text{ether})_n,Br_3^- \overset{K_d}{\rightleftharpoons} H^+(\text{ether})_n + Br_3^- \qquad (1a)$$

The extinction coefficient at 273 mμ for the DCC tribromide complex ($\epsilon = a/[Br_2]$), was determined to be 4.82×10^4. A threefold excess of DCC and HBr over bromine was used, all concentrations being in the range of 10^{-4}–$10^{-3}\ M$. The assumption of a total complexation of bromine under these conditions was verified by experiments, in which DCC was kept constant while increasing amounts of HBr and Br_2 were added (see plateau in Figure 2). The contribution of reaction 1a, dissociation into free ions, to the overall complexation is neglected, since the conductance measurements indicate that under the experimental conditions the fraction of free ions in the solution is still small. At 25° K_d for the DCC system is estimated to be about $10^{-7}\ M$.

Please note the agreement between the value of the extinction coefficient of the DCC complex, $\epsilon = a/[DCC]$, shown in Figure 2 for experiments in which $HBr + Br_2$ was in excess with ϵ derived from experiments in which an excess of DCC was used. Hence, a 1:1 stoichiometry for the complexation of DCC with hydrogen tribromide is evident.

The complexation of DCC with $Br_2 + HBr$ is apparently brought to completion even at very low concentrations of the reagents. On the basis of the initial deviation of the absorbance at 273 mμ from its plateau value, shown in Figure 2, we estimate that $K_{ov} > 10^9$.

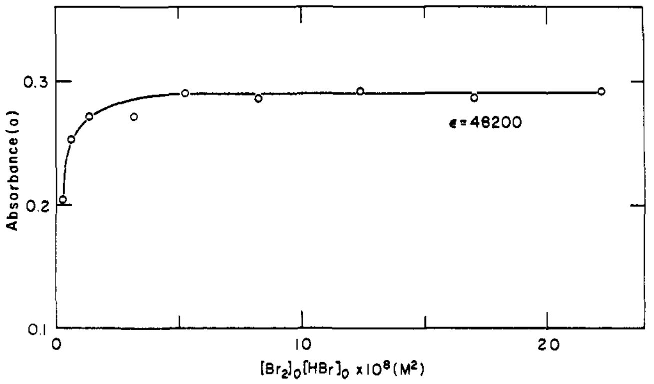

Figure 2. Absorbance at 273 mμ for a constant $[DCC]_0 = 6.07 \times 10^{-6}\ M$ and increasing concentrations of HBr and Br_2 in chloroform solutions at 25°. $[Br_2]_0/[HBr]_0 \approx 1$.

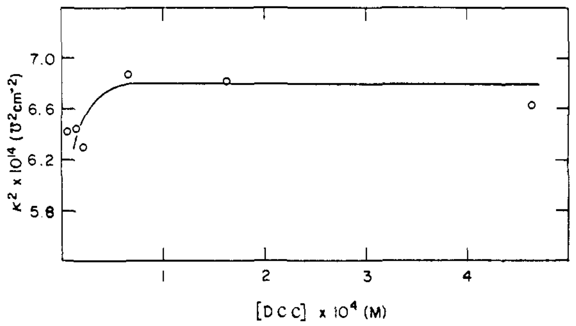

Figure 3. Specific conductance at 25° of hydrogen bromide in chloroform solutions as a function of an excess of DCC. $[HBr]_0 = 3.6 \times 10^{-5}\ M$.

The two consecutive steps[16] are involved in the overall reaction (1), namely

$$DCC + HBr \overset{K_p}{\rightleftharpoons} DCCH^+,Br^- \qquad (2)$$

and

$$DCCH^+,Br^- + Br_2 \overset{K_3}{\rightleftharpoons} DCCH^+,Br_3^- \qquad (3)$$

Reaction 2 represents the formation of an ionic complex from covalent reactants and may be followed by changes in conductance of the solutions. Specific conductances, κ's, of an HBr solution, were measured in the presence of increasing amounts of DCC. The plot of κ^2 *vs.* excess of DCC for $[HBr] = 3.6 \times 10^{-5}\ M$ is shown in Figure 3. Even at such low concentration of HBr a small excess of DCC suffices to bring the conductivity to its plateau.

K_p may be calculated from the initial dependence of κ on the concentration of DCC. Strictly speaking, values of κ are defined by the concentration of the $DCCH^+,Br^-$ ion pair, extent of its dissociation into free ions, and their mobility. For the narrow concentration range corresponding in our experiments to partial or total complexation of HBr with DCC, it may be assumed that the ionic mobilities are constant. Therefore, concentrations of free ions are proportional to κ's.

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(16) The reaction $DCC + Br_2 \rightleftharpoons DCC, Br_2$ may be neglected, since recent studies revealed[17] that the stability of such a molecular bromine complex is many orders of magnitude lower than that of the DCC–HBr complex.

(17) E. Shchori and J. Jagur-Grodzinski, *Isr. J. Chem.*, in press.

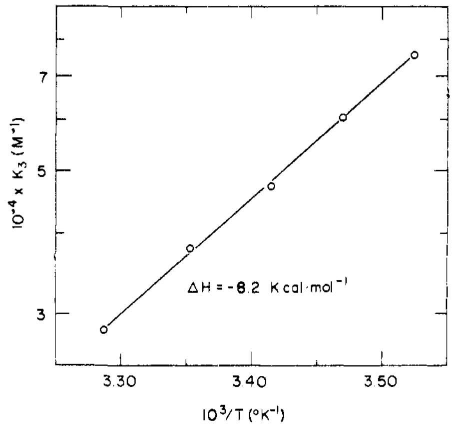

Figure 4. Semilog plot of K_3 *vs.* reciprocal absolute temperature. $[DCC]_0 = 5.20 \times 10^{-6}$, $[Br_2]_0 = 3 \times 10^{-5}\ M$, $[HBr]_0 = 3 \times 10^{-5}\ M$.

Since the concentrations of free ions are also proportional to the square roots of the concentrations of ion pairs, it follows that

$$\frac{[DCCH^+,Br^-]}{[HBr]_{max}} = \left(\frac{\kappa}{\kappa_{max}}\right)^2 \qquad (4)$$

where $[HBr]_{max}$ is the concentration of ion pairs when all HBr is complexed with DCC. Hence, $[HBr]_{max} = [HBr]_0(1 - \alpha)$. We estimate[18] that in our system $\alpha \approx 0.07$ and $[HBr]_{max} \approx [HBr]_0$. Accordingly, one derives from eq 2 and 4

$$K_p = \left\{\left(\left[\frac{\kappa_{max}}{\kappa}\right]^2 - 1\right)\left([DCC]_0 - [HBr]_0\left[\frac{\kappa}{\kappa_{max}}\right]^2\right)\right\}^{-1} \qquad (5)$$

Using values of κ^2 from Figure 3, one calculates from eq 5 $K_p^{25°} \sim 10^6\ M^{-1}$.

Complexation of DCC with HBr is therefore very strong, and it comes to completion at very low concentrations of the reagents. As a matter of fact, it was already completed under the conditions used in the spectrophotometric experiments described in the preceding paragraph. Changes in absorbance at 273 mμ observed in these experiments should, therefore, be attributed to reaction 3 only. Hence, $K_3^{25°} = 3.7 \times 10^4\ M^{-1}$ is calculated from the expression $K_3 = a/(\epsilon \cdot [DCC]_0 - a)([Br_2]_0 - a/\epsilon)$, where a is the absorbance at 273 mμ. Values of K_3 in the temperature range 10–31° were determined from experiments in which $[DCC]_0 = 5 \times 10^{-6}\ M$, $[Br_2]_0 = 10^{-5}\ M$, while HBr was in excess over DCC. From the plot of log K_3 *vs.* $1/T$ shown in Figure 4, one calculates $\Delta H = -8.2$ kcal/mol and $\Delta S = -6.6$ eu.

The extinction coefficients of complexes of other ethers with hydrogen tribromide were assumed to be identical with that of the $DCCH^+,Br_3^-$ complex. This assumption could be verified for glyme-3. One derives $\epsilon = 4.9 \pm 0.1 \times 10^4$ from experiments in which a large excess of glyme-3 (0.25 M) and HBr ($2 \times 10^{-2}\ M$) over Br_2 ($10^{-4}\ M$) was used. For other ethers, concentrations of the complexed species could thus be calculated from the 270–273-mμ absorption band assigned to the Br_3^- group. Such an assignment is supported by data reported in the literature for tetraalkylammonium tribromides in ethylene chloride.[20]

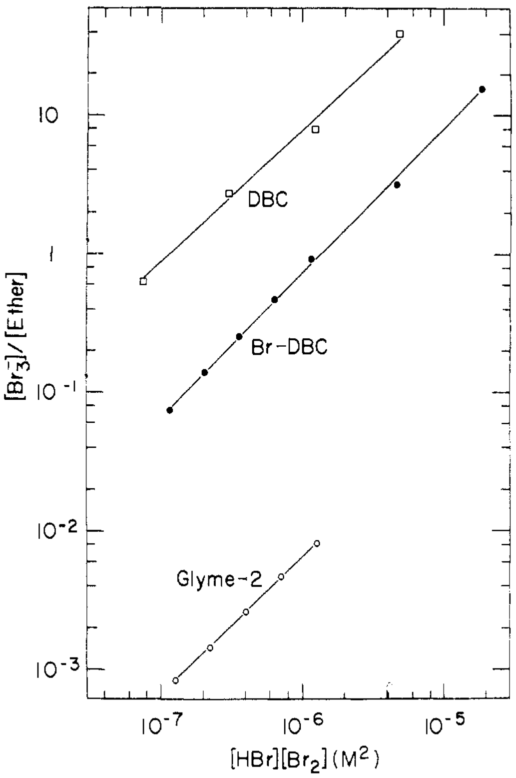

Figure 5. Log–log plots of $[Br_3^-]/[\text{ether}]$ *vs.* the excess of HBr and Br_2 in chloroform solutions at 25°.

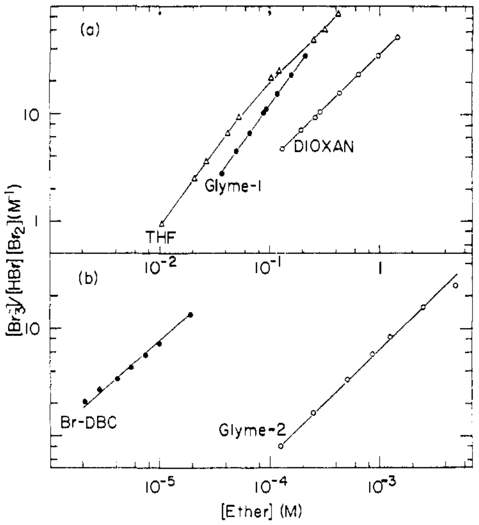

Figure 6. Log–log plots of $[Br_3^-]/[HBr][Br_2]$ *vs.* the excess of ether in chloroform solutions at 25°.

The equilibrium constants of complexation of DBC, Br-DBC, glyme-2, glyme-1, THF, and dioxane with hydrogen tribromide were determined by changing concentrations of HBr and Br_2 at a constant initial concentration of the respective ethers, as well as by changing the concentration of an ether while keeping $[HBr]_0$ and $[Br_2]_0$ constants.

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(18) Estimate of α is based on measurements of the concentration dependence of conductance of DCC complexes in chloroform and in other solvents,[14,19] which yield for $DCCH^+,Br^-$ in chloroform at 25° $\Lambda_0 = \lambda^+ + \lambda_0^- \sim 100$ and $K_d\Lambda_0^2 \approx 2.0 \times 10^{-3}$.

(19) E. Shchori, unpublished results from this laboratory.

(20) R. E. Buckles and J. P. Yuk, *J. Amer. Chem. Soc.*, **75**, 5048 (1953).

The experimentally determined concentrations of the Br_3^- complex were subtracted from the initial concentrations of the reagents, thus yielding their equilibrium concentrations. The log-log plots of the [complex] *vs.* equilibrium concentrations of the reagents are shown in Figures 5 and 6. Straight lines with a 45° slope are obtained for all macrocyclic ethers and for glyme-2, indicating a 1:1 stoichiometry of these complexes. Intercepts of plots shown in Figure 5 and Figure 6b yield the respective overall equilibrium constants (K_{ov}) of complexation at 25°, listed in Table II. In the case of glyme-1 and of THF, equilibrium constants cannot be calculated in this manner, since a deviation from the 1:1 stoichiometry is evident (see Figure 6a). A slope of about 1.4 is observed for glyme-1, while in the case of THF a slope of about 1.0 at the high concentration range gradually increases to 1.43 at lower concentrations of THF. For dioxane, a slope of 1.0 is again observed; however, for this ether, only its high concentration range was investigated.

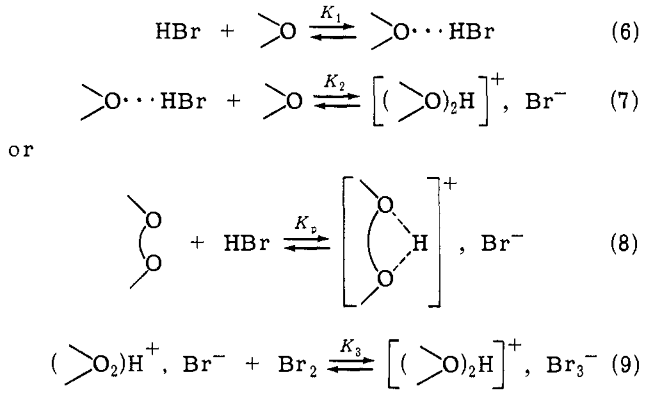
Table II. Complexations of Ethers with Hydrogen Bromide and Hydrogen Tribromide in Chloroform at 25°

Ether	$K_{ov} = K_pK_3$, M^{-2}	K_p, M^{-1}	
DCC	$>10^9$	10^6	
DBC	7.8×10^6	210^a	
Br-DBC	7.2×10^5	20^a	
Glyme-3	7.6×10^3	0.20^a	
Glyme-2	6.4×10^3	0.17^a	
	K_2K_3, M^{-2}	K_2,[b] M^{-1}	K_1, M^{-1}
Glyme-1	222	6.0×10^{-3}	13
THF	235	6.3×10^{-3}	48.5
Dioxane	35	0.95×10^{-3}	

[a] Calculated from K_{ov} for $K_3 = 3.7 \times 10^4\ M^{-1}$. [b] Calculated from K_2K_3 for $K_3 = 3.7 \times 10^4\ M^{-1}$.

Apparently, the ionic tribromide complex is formed only when two oxygens interact with the hydrogen atom. The monobasic complex halogen acids were indeed shown to include two ethereal molecules.[21]

The following mechanism accounts for the experimental findings.



$$\text{HBr} + {>}\text{O} \underset{}{\overset{K_1}{\rightleftharpoons}} {>}\text{O}\cdots\text{HBr} \qquad (6)$$

$${>}\text{O}\cdots\text{HBr} + {>}\text{O} \overset{K_2}{\rightleftharpoons} \left[({>}\text{O})_2\text{H}\right]^+,\ \text{Br}^- \qquad (7)$$

or

$$\text{(glyme)} + \text{HBr} \overset{K_p}{\rightleftharpoons} [\ ]^+,\ \text{Br}^- \qquad (8)$$

$$({>}\text{O}_2)\text{H}^+,\ \text{Br}^- + \text{Br}_2 \overset{K_3}{\rightleftharpoons} \left[({>}\text{O})_2\text{H}\right]^+,\ \text{Br}_3^- \qquad (9)$$

In the proposed scheme, the experimentally observed orders of complexation of $HBr + Br_2$ with glyme-1 or with THF are rationalized by the assumption that the first step of the interaction, between these ethers and HBr, involves formation of a nonionic hydrogen-bonded species, which does not participate in the formation of the tribromide complexes (see eq 6). Such an assumption is consistent with the observation that the solubility of HBr in chloroform is greatly enhanced by the addition of THF, while its effect on the conductance of the solution is very small (see Table I).

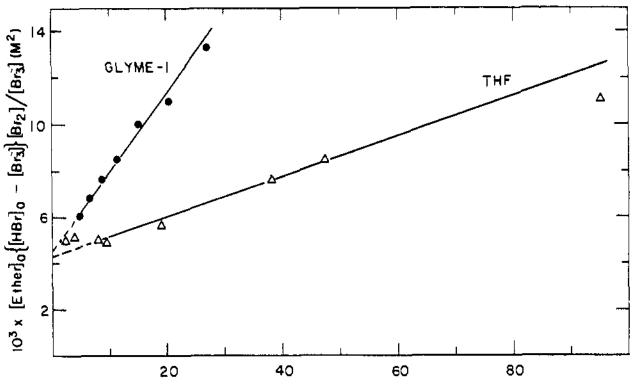


Figure 7. (Δ) $[HBr]_0 \approx 0.79 \times 10^{-3}\ M$, $[Br_2]_0 = 1.88 \times 10^{-3}\ M$, complexing ether, THF; (●) $[HBr]_0 \approx 1.1 \times 10^{-3}\ M$, $[Br_2]_0 = 0.32 \times 10^{-3}\ M$, complexing ether, glyme-1.

For $[\text{ether}]_0 \gg [\text{HBr}]_0$ eq 6, 7, and 9 yield

$$K_2K_3 = [\text{Br}_3^-]\{1/K_1 + [\text{ether}]_0\}/[\text{ether}]_0^2 \times \{[\text{HBr}]_0 - [\text{Br}_3^-]\}[\text{Br}_2] \qquad (10)$$

where $[Br_3^-]$ stands for $[(>O)_2H^+,Br_3^-]$ and $[Br_2] = \{[Br_2]_0 - [Br_3^-]\}$. Hence, for $[\text{ether}]_0 \gg 1/K_1$, an apparent first-order relationship is observed, while a second-order dependence on ether concentration is expected for $[\text{ether}]_0 \ll 1/K_1$. An expression convenient for graphic representation is derived by rearranging eq 10.

$$[\text{ether}]_0\{[\text{HBr}]_0 - [\text{Br}_3^-]\}[\text{Br}_2]/[\text{Br}_3^-] = 1/K_1K_2K_3[\text{ether}]_0 + 1/K_2K_3 \qquad (11)$$

From slopes and intercepts of straight lines obtained from such plots for glyme-1 and THF (see Figure 7), the respective values of K_1 and K_2K_3 are calculated. One finds that $K_1^{\text{THF}} > K_1^{\text{glyme-1}}$ in agreement with the order of basicities of oxygens in these ethers[22] as determined by their ir shifts due to hydrogen bonding with CH_3OD ($\Delta\nu_{OD}^{\text{THF}} = 115\ \text{cm}^{-1}$, $\Delta\nu_{OD}^{\text{glyme-1}} = 93\ \text{cm}^{-1}$). The proposed mechanism, based on assignment of K_1 to hydrogen bonding between one ethereal group and HBr molecule is, therefore, self-consistent. A linear alignment, similar to that in hydrogen-bonded water,[23] of two oxygens with the proton, is apparently required in order to convert the predominantly covalently bonded HBr molecule into a polar ion pair. Since the distance between properly aligned atoms must certainly be larger than 2.76 Å (the distance between oxygens in ice crystals), two molecules of the bifunctional glyme-1 are still required, but only one glyme-2 molecule suffices. In the macrocyclic "crown" ethers used in our experiments, such an alignment may be achieved without any significant loss of the entropy of the system. Moreover, since two oxygens in the macrocyclic ring are fixed at a distance of 3.5–4.0 Å, they may be expected to in-

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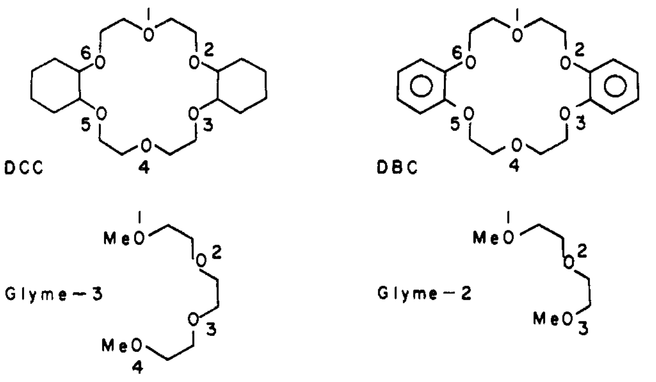

Figure 8.

teract simultaneously with the HBr molecule, hence, their effectiveness. Ethereal oxygens separated by a chain of five atoms are apparently involved in such interaction (*e.g.*, oxygens 1 and 3 in Figure 8). This conclusion is based on the observation that the effectiveness of glyme-2 as complexing agent is comparable to that of glyme-3, *viz.*, $K_{ov}^{\text{glyme-3}}/K_{ov}^{\text{glyme-2}} = 1.2$. One might expect that glyme-3 would act as a much stronger complexing agent than glyme-2 if interaction of HBr with oxygens, separated by a chain of eight atoms, had been preferable. Simultaneous participation of oxygen atoms 1 and 4 in the complexation of HBr may also be ruled out, as inconsistent with the large difference between the complexing power of DCC and DBC, since the basicity of these oxygens is comparable in the two ethers.

The equilibrium constant of complexation of Br_2 with the complexed hydrogen bromide ion pair was assumed to be negligibly affected by the nature of ether interacting with HBr. Thus, the value of $K_3 = 3.7 \times 10^4$ M^{-1}, which was determined for the $DCCH^+,Br^- + Br_2$ system at 25°, was used for the calculation of K_p's and K_2's from the experimentally determined K_{ov} and K_2K_3. The pertinent values are listed in Table II. The comparison of values of K_1's and K_2's listed in Table II reveals that hydrogen bonding represents the predominant interaction of HBr with THF and glyme-1.

Plots of log K_{ov} *vs.* $1/T$ shown in Figure 9 yield enthalpies and entropies of complexation with glyme-2 and Br-DBC. The relatively high values of $-\Delta H$ (17.1 and 14.8 kcal mol^{-1}, respectively) are due to the fact that they represent a sum of two consecutive reactions. The enthalpies of protonation by HBr may be calculated by subtracting the heat of complexation of Br_2 with the Br^- ion pair from these values, *viz.* $-\Delta H_{\text{glyme-2}} = 8.9$ kcal/mol and $-\Delta H_{\text{Br-DBC}} = 6.6$ kcal/mol. $-\Delta H_{\text{glyme-2}} > -\Delta H_{\text{Br-DBC}}$ is in accordance with the respective basicities of oxygen atoms in these ethers.

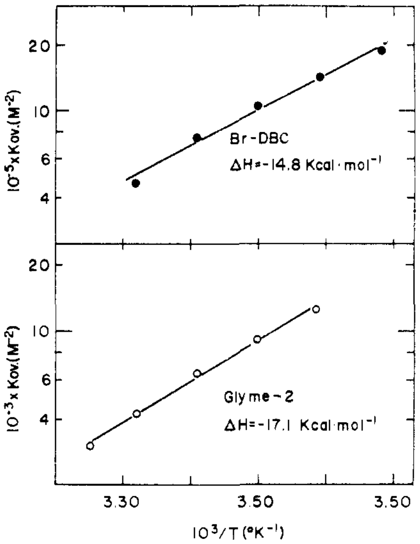

Figure 9. Semilog plots of K_{ov} *vs.* reciprocal absolute temperature: (●) complexing ether, Br-DBC; (○) complexing ether, glyme-2.

The entropy of complexation of Br-DBC + Br_2 + HBr ($\Delta S = -23$ eu) corresponds to the loss of translational and rotational freedom of two molecules, while for glyme-2 ($\Delta S = -40$ eu) a considerable restriction of freedom of segmental movements is also evident. The very high complexing power of DCC is apparently due to the combination of a relatively high basicity of this aliphatic ether with the low entropy of complexation.

Finally, one may predict that an even stronger complexation of acids with ethers may be achieved by fixing the properly aligned oxygens in a macrocyclic ring at an even shorter distance than in DCC. The separation of ethereal groups in the ring by more than two carbons should also be beneficial, since the basicity of the resulting ethers will thus be increased.