oxygen atom into line in order to link the tetrahedra through a corner and form a siloxane linkage. This deformation could conceivably produce islands of geminal hydroxyls which remain after annealing.

In conclusion, the results reported here for both the annealed and rehydrated Cabosils tend to support the model postulated by Peri and Henseley.[17] However, their picture for the former surface is probably an oversimplified view of the real structure.

Alumina. The unit cell of γ-Al_2O_3 can be represented as a cube of side 7.84 Å, presenting eight oxide ions at each face. It has a defect spinel structure,[23,24] with 21.33 Al atoms arranged at random in the 16 octahedral and 8 tetrahedral vacancies. Chemisorption of water molecules saturates all the available oxide ions, giving a surface equivalent to that of gibbsite. This is consistent with the X-ray findings.[25] There are 17 hydroxyls[26] per 100 Å^2 of surface; the average distance separating the hydroxyls here is particularly favorable for reaction of two neighboring groups with VCl_4. The actual observed hydroxyl content of the Alon sample is 2.8 mmol g^{-1}. The theoretical value is 2.17 mmol g^{-1} for 100 m^2 g^{-1} of surface area (n = 13.1), assuming each oxide ion at the surface reacts with H_2O to form a hydroxide ion. Therefore, nonsurface hydroxyls may be present in the sample.

The maximum epr intensity was attained at about 10% coverage on γ-Al_2O_3 as compared to about 40% on Cabosil. The surface concentration of vanadium atoms is nearly the same at 10% coverage on alumina as that at 30% coverage on rehydrated Cabosil.

All the paramagnetic probes are doubly attached to the alumina surface as shown by the stoichiometry of HCl evolution. Therefore, the vanadium atoms in this surface are immobile. In consonance with this conclusion, heating the samples to 450° causes no decrease in epr intensities and line broadening of the spectra is a function of coverage only and is independent of temperature.

That the surface of boehmite is different from those of gibbsite and γ-Al_2O_3 has already been demonstrated by adsorption experiments.[22] Both oxide and hydroxide ions are found on the surface of boehmite having layered patterns. The epr spectra indicate that the paramagnetic probe in this case has rhombic symmetry. It is possible that the presence of oxide ions in the surface provides weak additional ligand-field perturbations of the vanadium atoms.

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(23) G. Hägg and G. Söderholm, *Z. Phys. Chem., Abt. B*, **29**, 88 (1935).

(24) E. Kordes, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **91**, 193 (1935).

(25) B. Imelik, *C. R. Acad. Sci.*, **223**, 1284 (1951).

(26) J. J. Kipling and D. B. Peakall, *J. Chem. Soc.*, 834 (1957).

Salt Complexes of Cyclic Polyethers. Distribution Equilibria

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Abstract: Partition of salt complexes of cyclic polyethers between water and immiscible solvents has been used extensively as a measure of complexing tendency. It was the aim of the present work to establish the equilibria governing these processes and to analyze them in terms of the underlying molecular processes. Published data and new data on alkali–picrate complexes of two cyclic polyethers (18-membered polyether rings containing 6 oxygens) are utilized to establish the functional form of the overall equilibrium and the equilibrium constants. The overall equilibrium is analyzed in terms of three constituent equilibria: complex formation in the aqueous phase and partition of uncomplexed polyether and of complex. It has also been possible to deduce equilibrium constants for the dissociation of complex cation–picrate ion pairs in the organic solvent. Though the constants are small, they indicate considerably more dissociation for the complex ion pairs than for the corresponding uncomplexed salt ion pairs.

The cyclic polyethers described by Pedersen are of special interest because of their remarkable complexing properties.[1,2] They form complexes with many salts, especially those of alkali and alkaline earth cations, both in solution and in the crystalline state. In a complex of the typical polyether (Figure 1), the cation is located in the center of the main ring in the plane, or almost in the plane, of the oxygen atoms,[3] being held there principally by electrostatic, *i.e.*, ion–dipole forces.[1]

Complexing in solution can be detected in many different ways, such as spectral changes, altered solubilities, and electrochemically. Complexing equilibrium

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(1) (a) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1767); (b) *ibid.*, **92**, 386 (1970).

(2) (a) C. J. Pedersen, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968); (b) *J. Amer. Chem. Soc.*, **92**, 391 (1970).

(3) D. Bright and M. R. Truter, *Nature (London)*, **225**, 176 (1970); *J. Chem. Soc. B*, 01544 (1970); M. A. Bush and M. R. Truter, *Chem. Commun.*, 1439 (1970).

constants (stability constants) for a number of systems have been measured potentiometrically,[4] calorimetrically,[5] and by spectroscopy.[6]

One less direct method for assaying the complexing tendency of various polyether–salt systems was devised and extensively used by Pedersen:[2] an aqueous solution of the salt, usually a picrate, in the presence of excess hydroxide is allowed to contact a solution of the polyether in an immiscible organic solvent, and the equilibrium distribution of the salt between the two phases is determined. The extent to which the salt is extracted into the organic phase is taken as a measure of complexing. Even though the extent of extraction evidently depends not only on the complexing equilibria but also on the solubilities and partition coefficients of the various uncomplexed and complexed species, this method has proved to be very convenient for rapid screening and has led to conclusions with regard to the effects of such factors as ring size and cationic size on complexing which are consistent with those derived from other measurements.[1,2]

Not only has this method turned out to be of great use in investigating complexing of salts by cyclic polyethers,[2,7] but it has also been applied to other neutral macrocyclic molecules. Eisenman, *et al.*,[7,8] have used picrate extraction for an extensive investigation of alkali cation complexing by the macrotetrolide actin antibiotics, which contain 32-membered polyether–polyester rings and which make phospholipid bilayer membranes selectively permeable to cations.

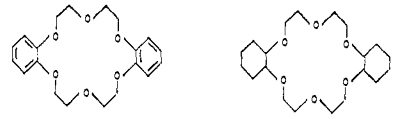
It is the purpose of the present study to show that such extraction results can be expressed in terms of simple equilibria which throw some light on the molecular processes involved.

Experimental Section

Cyclic Polyethers. The two cyclic polyethers used in this work (Figure 1) were prepared by Pedersen's methods.[1a] Dibenzo-18-crown-6 was purified by recrystallization from toluene.

Dicyclohexyl-18-crown-6, which is made by hydrogenation of the dibenzo analog, has the possibility of cis–trans isomerism at the two bridge bonds, but nmr spectra suggest that all the bridge hydrogens are equatorial, *i.e.*, that both bridge bonds are trans.[9] This conclusion is consistent with the fact that only two isomers are found,[10] presumably a meso and a *dl* form. The sample of the isomeric mixture used in some of the measurements reported here contained roughly equal parts of the two isomers.

The pure isomers of dicyclohexyl-18-crown-6 were prepared by column chromatography on Al_2O_3 (Woelm neutral).[10] The polyether was placed on the column as an *n*-hexane solution (5 g of polyether in 10 ml of *n*-hexane per 100 g of Al_2O_3) and eluted with 20/80 vol/vol ether–*n*-hexane. After elution of about 30–40% of the polyether, the eluate was freed of solvent. The resulting polyether was crystallized from *n*-hexane and then rechromatographed on a smaller column and finally recrystallized from *n*-hexane at 0° to give material with no impurities detectable by tlc (mp 61–62.5°, designated isomer A). The remaining material was stripped off the column with methanol. The strippings, after removal of solvent, were recrystallized twice from *n*-hexane, in which this isomer was considerably less soluble than isomer A (mp 69–70°, designated isomer B).[11]



I II

Figure 1. Structural formulas of cyclic polyethers: I, dibenzo-18-crown-6,6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]-hexaoxacyclodecine; II, dicyclohexyl-18-crown-6, eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclodecine.

Extraction Procedure. The aqueous solutions were made up from standardized stock solutions of NaOH, KOH, and picric acid. The polyether was dissolved in the organic phase. Equal volumes of the two solutions in screw-cap Erlenmeyer flasks were thoroughly agitated on a Vortex Junior mixer for at least 1 min, which was found to be sufficient for equilibration. Generally the phases separated cleanly on standing, though centrifugation was necessary in some instances. All extractions were conducted in a constant-temperature room at 25.5 ± 0.5°. Concentration ranges for the most extensively investigated system are indicated in the captions of Figures 2 and 3. Those of the other systems were similar.

Equilibrium picrate concentrations in both phases were determined with a Cary 14 spectrophotometer. The two values of the picrate concentration in the organic phase, *A*, (the direct value and that obtained by difference from the aqueous concentration) agreed well and were averaged for use in the further calculations. The aqueous picrate extinction coefficient (1.45×10^4 cm^{-1} M^{-1} at 354 nm) was determined by direct calibration with solutions containing excess base. The organic extinction coefficients (1.80×10^4 cm^{-1} M^{-1} at 370 nm for CH_2Cl_2, 1.64×10^4 at 350 for $CFCl_2CF_2Cl$) were obtained from preliminary extraction runs in which the picrate concentration in the organic phase was taken to be the difference between the total and the aqueous concentrations. The *n*-hexane data were obtained by Eisenman.[12]

Solubility of the Polyethers. Water solubilities of the dicyclohexyl-18-crown-6 isomers, determined by equilibration at 25.0° for up to 9 days, drying, and weighing, were found to be 0.053 *M* for isomer A, 0.018 *M* for isomer B.

Partition coefficients between organic solvents and water were determined by equilibration of the two phases as in the extraction procedure, followed by analysis of the aqueous layer by picrate extraction. For this purpose KOH (0.05 *M*) and picric acid (0.005 *M*) were added to an aliquot, which was then extracted with an equal volume of methylene chloride. As can be shown by means of the extraction equilibrium constants reported below, more than 99% of the polyether is extracted at these concentrations and an equivalent quantity of picrate accompanies it. Thus spectrophotometric picrate analysis of the methylene chloride extract yields the concentration of polyether in the aqueous phase, which is often quite low. Partition coefficients were determined in this way at a number of concentrations between 0.01 and 0.1 *M* in the organic phase. The average values, recorded in Table I, are considered reliable to about 10%.

Table I. Partition Coefficients of Dicyclohexyl-18-crown-6

	P_e[a]	
Organic phase	Isomer A	Isomer B
CH_2Cl_2	2.5×10^{-4}	2.7×10^{-4}
$CFCl_2CF_2Cl$	8.2×10^{-2}	6.0×10^{-2}
n-C_6H_{14}	1.6×10^{-1}	1.4×10^{-1}

[a] As defined by eq 7.

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(4) H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971).

(5) R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore, and J. J. Christensen, *Science*, **164**, 443 (1969); R. M. Izatt, D. P. Nelson, J. H. Rytting, and J. J. Christensen, *J. Amer. Chem. Soc.*, **93**, 1619 (1971).

(6) K. H. Wong, G. Konizer, and J. Smid, *ibid.*, **92**, 666 (1970).

(7) G. Eisenman, S. M. Ciani, and G. Szabo, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, 27, 1289 (1968).

(8) G. Eisenman, S. Ciani, and G. Szabo, *J. Membrane Biol.*, **1**, 294 (1969).

(9) E. G. Brame, in preparation.

(10) Dr. D. J. Sam devised the isomer separation procedure and first established the existence of the two isomers.

(11) A sample of the slower migrating isomer obtained by essentially the same chromatographic procedure (by R. M. Izatt and B. L. Haymore, Brigham Young University, and kindly supplied by them to us) had a considerably higher melting point, 83–84°. However, it was found to be a polymorph of isomer B, as demonstrated by (1) identical solution properties (stability constant for K^+ in methanol, nmr, and tlc), (2) no melting point lowering on mixing, and (3) interconversion by seeding of supercooled melt or supersaturated solution.

(12) G. Eisenman, private communication.

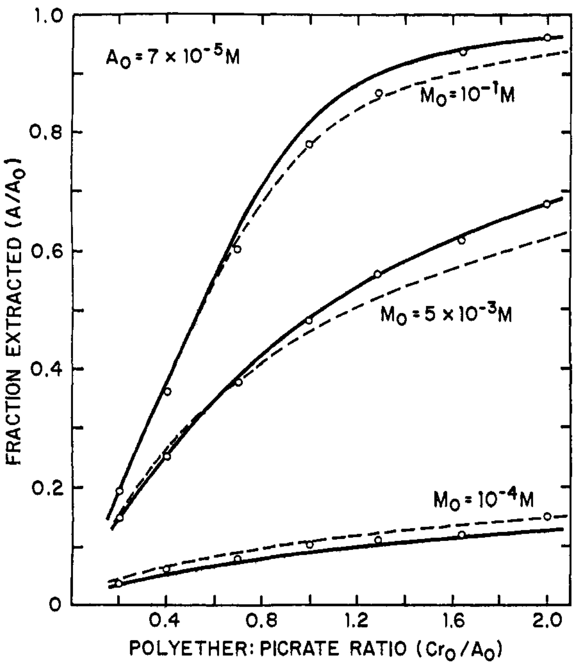

Figure 2. Extraction of potassium picrate into methylene chloride by dicyclohexyl-18-crown-6. Picrate concentration $[A_0] = 7 \times 10^{-5}$ *M*. Points observed are from ref 2a. Curves were calculated by eq 5 and 9–12: full curves, $K_e = 2.1 \times 10^6$ M^{-2} and $K_d = 3.7 \times 10^{-5}$ *M*; dashed curves, $K_eK_d = 160$ M^{-1} and $K_d = \infty$.

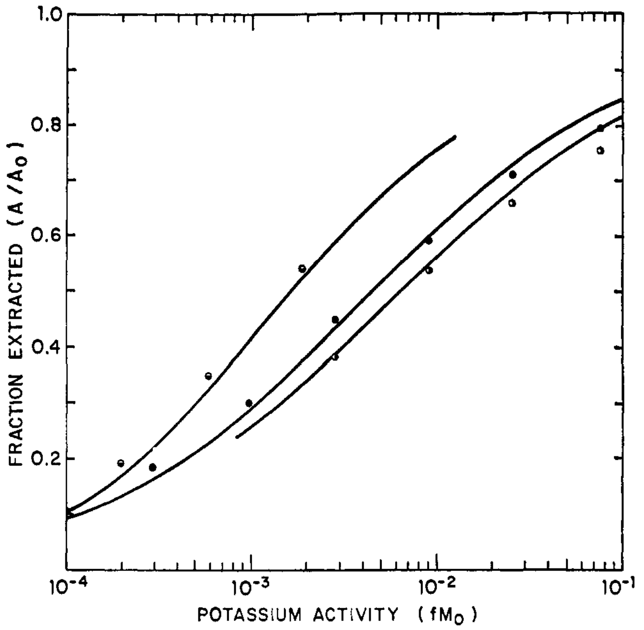

Figure 3. Extraction of potassium picrate into methylene chloride by dicyclohexyl-18-crown-6. Polyether:picrate ratio $[Cr_0]/[A_0] = 1.00$. Polyether concentration $[Cr_0]$: ◑, 4.6×10^{-5} *M*; ●, 9.2×10^{-5} *M*; ◒, 4.6×10^{-4} *M*. Points were observed. Curves were calculated by eq 5 and 9–12; $K_e = 2.1 \times 10^6$ M^{-2}, $K_d = 3.7 \times 10^{-5}$ *M*.

Results and Discussion

The Overall Extraction Equilibrium. The equilibrium between an aqueous solution containing alkali cation (M^+), picrate ion (A^-), and hydroxide ion, and an organic solution containing a cyclic polyether (Cr) can be formulated as

$$M^+_{aq} + A^-_{aq} + Cr_{org} \overset{K_e}{\rightleftharpoons} MCrA_{org} \tag{1}$$

where MCrA designates ion pairs (alkali–polyether cations, MCr^+, and picrate anions) in the organic phase. If the organic phase is polar enough and the concentration low enough, these ion pairs will partly dissociate according to

$$MCrA_{org} \overset{K_d}{\rightleftharpoons} MCr^+_{org} + A^-_{org} \tag{2}$$

Two further equilibria have to be included in order to account for the distribution of all the components. One is the partition of uncomplexed polyether between the two phases

$$Cr_{org} \overset{P_e}{\rightleftharpoons} Cr_{aq} \tag{3}$$

As shown by the partition coefficients in Table I, the concentration of the polyether in the aqueous phase is negligible only for CH_2Cl_2 but not for the other solvents. The other equilibrium involves complexing in the aqueous phase, which must also be taken into account if the aqueous polyether concentration is appreciable

$$M^+_{aq} + Cr_{aq} \overset{K_s}{\rightleftharpoons} MCr^+_{aq} \tag{4}$$

Independent measurements of this equilibrium have been published previously.[4,5]

Equilibrium constants corresponding to the reactions of eq 1–4 are defined as

$$K_e = [MCrA]_{org}/([M^+]_{aq}[A^-]_{aq}[Cr]_{org}) \tag{5}$$

$$K_d = [MCr^+]_{org}[A^-]_{org}/[MCrA]_{org} \tag{6}$$

$$P_e = [Cr]_{aq}/[Cr]_{org} \tag{7}$$

$$K_s = [MCr^+]_{aq}/[M^+]_{aq}[Cr]_{aq} \tag{8}$$

where the brackets denote equilibrium activities.

Blank experiments showed no detectable extraction in the absence either of picrate or of polyether[2a] so that the concentrations of hydroxide ion and uncomplexed alkali picrate in the organic phase could be neglected. The activity coefficient of aqueous alkali ion was taken into account. All other activity coefficients were taken to be unity, since they refer to neutral species or to ions at concentrations below 10^{-4} *M*. The 1:1 stoichiometry of the complexes involved in this work has been amply demonstrated.[1–5]

The necessary activities are given by the following relations

$$[M^+]_{aq} = f(M_0 - A) \tag{9}$$

$$[A^-]_{aq} = A_0 - A \tag{10}$$

$$[Cr]_{org} = (Cr_0 - A)/[1 + P_e + P_eK_sf(M_0 - A)] \tag{11}$$

$$[MCrA]_{org} = [2A + K_d - (K_d^2 + 4K_dA)^{1/2}]/2 \tag{12}$$

where f is the single-ion activity coefficient of the aqueous cation. The second or third terms in the denominator of eq 11 account for polyether in $[Cr]_{aq}$ and $[MCr^+]_{aq}$. Equation 12 comes from the simultaneous solution of eq 6, the stoichiometric relation $A = [MCrA]_{org} + [A^-]_{org}$, and the neutrality condition $[A^-]_{org} = [MCr^+]_{org}$. Equal volumes of the two phases,

Table II. Picrate Extraction Equilibrium Constants

Polyether	Cation	Solvent	No. of points	$K_e \times 10^{-3}$, M^{-2} [a]	$K_d \times 10^{6}$, M [a]
Dicyclohexyl-18-crown-6					
Mixed isomers	K^+	CH_2Cl_2	26[b]	2100 ± 200	37 ± 6
Isomer A	K^+	CH_2Cl_2	5	4000 ± 500	25 ± 8
Isomer B	K^+	CH_2Cl_2	5	1100 ± 150	24 ± 8
Mixed isomers	K^+	$CFCl_2CF_2Cl$	14	19 ± 2	<1[d]
Mixed isomers	K^+	n-C_6H_{14}	9[c]	3.8 ± 0.2	<1[d]
Mixed isomers	Na^+	CH_2Cl_2	9	15 ± 2	100 ± 20
Dibenzo-18-crown-6	K^+	CH_2Cl_2	9	710 ± 60	4.4 ± 2.7

[a] The ± values are 95% confidence limits from the nonlinear regression analysis. [b] Results from this work pooled with those of Pedersen.[13] [c] Results of Eisenman.[12] [d] Zero lies within 95% confidence limits.

such as were used in all experiments, are implicit in the expression.

Substitution of eq 9–12 into eq 5 gives a single relation with two unknowns, K_e and K_d. The latter were evaluated by nonlinear regression fitting of 5–26 data points per system, the deviation of the measured variable A being minimized in the process. Points at $M_0 = 0.1\ M$ were omitted from the regression analysis, since they invariably deviated a great deal more from the predicted curves than those at lower concentrations, possibly owing to activity coefficient deviations.

Data over wide concentration ranges are necessary to test the validity of the above equilibrium expressions. Among all the previously published results there is only one set[13] of points (shown in Figure 2) covering broad ranges of cation and polyether concentrations but all at the same picrate concentration. However, new data at different picrate concentrations (shown in Figure 3) had to be obtained to make possible reliable estimates of K_d. Data at constant picrate concentration are insensitive to K_d, as shown by the fact that the points in Figure 2 can be fitted almost as well on the assumption of partial ion pairing (full curves) as on the basis of complete dissociation (dashed curves). On the other hand, the data of Figure 3 rule out complete dissociation, which would require all the points at constant polyether:picrate ratio to fall on a single curve regardless of picrate concentration.

As described above, best estimates of K_e and K_d were obtained by a regression technique. The quality of agreement between observed and predicted data is illustrated in Figures 2 and 3, in which 35 points covering very wide concentration ranges of the three components are fitted very well with only two adjustable parameters. This indicates that equilibria 1 and 2 are indeed adequate to represent the processes which occur. Similar agreement was also obtained for the other systems. As shown in Table II, the regression fitting gives K_e within 10% confidence limits and K_d within 20–30% except for the very low values.

The extraction equilibrium constants in Table II describe quantitatively how much more efficient methylene chloride is for extraction of the polyether–picrate complex than the less polar solvents, how dibenzo-18-crown-6 is less efficient than its saturated analog, and how sodium ion is much less extracted than potassium. These effects not only reflect strength of complexing but also involve the solubilities of the various species, as will be discussed in the next section. However, knowledge of the equilibrium constants permits predictions of the effects on extraction of varying the different concentrations. For instance, it was possible to specify conditions for the quantitative determination of the cyclic polyether by extraction of an equivalent quantity of picrate (see Experimental Section).

Most of the runs in Table II used the isomeric mixture of dicyclohexyl-18-crown-6. It is, of course, not strictly valid to treat this as a single molecular species with intermediate properties for purposes of determining equilibrium constants. However, as shown above, the equilibrium expressions could be fitted satisfactorily, and K_e for the isomeric mixture was just about halfway between the values for the two isomers, while K_d was the same within experimental error.

The dissociation constants are small, yet they indicate considerable dissociation of ion pairs in methylene chloride at the submillimolar concentrations of the experiments. Much less dissociation is expected for uncomplexed salts, but evidently in the complex the bulky polyether ring shields the charge of the cation very effectively and thus decreases the interionic attraction. Conductivity measurements demonstrated the same effects: a 0.001 M solution of KCl in 90/10 $CHCl_3$–CH_3OH had an equivalent conductance of less than 0.2 ohm^{-1} cm^2 mol^{-1}, which rose to 11.5 on addition of 1 equiv of dicyclohexyl-18-crown-6.

The Constituent Equilibria. The overall extraction equilibrium is too complex to permit unraveling of the specific molecular effects. However, it may be analyzed in terms of three constituent equilibria which, when added to each other, give eq 1.

$$M^+_{aq} + Cr_{aq} \overset{K_s}{\rightleftharpoons} MCr^+_{aq} \tag{13}$$

$$Cr_{org} \overset{P_e}{\rightleftharpoons} Cr_{aq} \tag{14}$$

$$MCr^+_{aq} + A^-_{aq} \overset{P_c}{\rightleftharpoons} MCrA_{org} \tag{15}$$

The three equilibrium constants are K_s, the aqueous stability constant of the cation complex, P_e, the partition coefficient of the polyether, and P_c, the partition coefficient of the complex from separate ions in the aqueous to ion pairs in the organic phase. Thus the overall extraction equilibrium constant is given by

$$K_e = K_s P_e P_c \tag{16}$$

Though P_c cannot be measured directly, it can be deduced whenever independent measurements of the three other constants are available. The P_c values in Table III were thus calculated by eq 16 from previously published stability constants[4,5] together with P_e and K_e results from Tables I and II. Table III also lists the alternative partition coefficient, $P_c K_d$, which corresponds

(13) Table III of ref 2a.

Table III. Equilibrium Constants for Extraction of Picrate with Dicyclohexyl-18-crown-6

Isomer	Cation	Solvent	K_e, M^{-2}	K_s,[a] M^{-1}	P_e	P_c, M^{-1}	P_cK_d
A	K^+	CH_2Cl_2	4.0×10^6	1.5×10^2	2.5×10^{-4}	1.1×10^8	3×10^3
B	K^+	CH_2Cl_2	1.1×10^6	6.0×10^1	2.7×10^{-4}	7×10^7	2×10^3
Mixture	K^+	$CFCl_2CF_2Cl$	1.9×10^4	1×10^2 [b]	7×10^{-2}	2.7×10^3	
Mixture	K^+	n-C_6H_{14}	3.8×10^3	1×10^2 [b]	1.5×10^{-1}	2.5×10^2	
Mixture	Na^+	CH_2Cl_2	1.5×10^4	4×10^1 [b]	2.6×10^{-4}	1.5×10^6	1.5×10^2

[a] From ref 4. [b] Average values.

to the reaction

$$MCr^+_{aq} + A^-_{aq} \rightleftharpoons MCr^+_{org} + A^-_{org} \qquad (17)$$

and is relevant when the complex ion pairs are largely dissociated in the organic phase.

The equilibrium constants in Table III give some insight into the effect of the solvent on extraction. While the overall equilibrium constant K_e decreases in the solvent sequence $CH_2Cl_2 \rightarrow CFCl_2CF_2Cl \rightarrow C_6H_{14}$, the partition coefficients of the complex, P_c or P_cK_d, decrease even more dramatically through more than six decades, and thus appear to be the dominating influence. The partition coefficient of the polyether, P_e, works in the opposite direction, since the lower polyether solubility in the less polar solvents actually furthers complexing in the aqueous phase. The difference in K_e of the two isomers is only partly due to strength of complexing, as measured by K_s, for the partition coefficients of their complexes also vary measurably. Similarly, the less efficient extraction of sodium compared to potassium is in large part caused by the partition coefficient, which is almost two decades lower, and only in small part by weaker complexing, which accounts for less than a factor of three.

The above considerations demonstrate how very important the solubility relations are in determining extraction properties and that strength of complex formation, while no doubt important, is not necessarily the governing factor. All the measurements reported here concern one anion, picrate, but it is evident that the very strong anion effect (*e.g.*, no measurable extraction of hydroxide or fluoride[2a]) comes from its effect on the complex partition coefficient.

The absolute magnitude of the partition coefficients leads to some interesting conclusions. The picrate complexes in the form of ion pairs are far more soluble in methylene chloride and moderately more soluble in the two less polar solvents than they are in water. Indeed this is the principal reason why extraction occurs. What is more noteworthy, however, is that even the dissociated ions of the picrate complex are considerably more soluble in methylene chloride than in water (*cf.* P_cK_d in Table III).

Acknowledgments. A considerable debt is owed to Charles J. Pedersen, who laid the foundations for this work and assisted it with much sage counsel. The author also wishes to acknowledge the assistance of the following colleagues: Paul J. Bente, III, who obtained much of the extraction data; D. J. Sam, who helped with the isomer separation; E. G. Brame, who provided the nmr information; and B. F. Winkel, who undertook the nonlinear regression analysis. Professor G. Eisenman, University of California, Los Angeles, contributed unpublished data and informative discussions.

Spectroscopy of Carbon Molecules. IV. C_4, C_5, C_6 (and C_9)[1]

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Abstract: The carbon molecules C_4, C_5, C_6, and perhaps C_9, have been formed in argon matrices by the reaction of C, C_2, and C_3. Highly enriched ^{13}C graphite was vaporized to form the isotopically substituted molecules. Analysis of the ir spectra of "pure" and mixed-isotope molecules made possible definite vibrational assignments for the Σ_u^+ frequencies. For $^{12}C_4$, $^{12}C_5$, and $^{12}C_6$ these are 2164; 1952, 1544; and 1997, 1197 cm^{-1}, respectively. The data on each molecule, including mixed-isotope species, were used to calculate stretching force constants. C_4 was found to have a strong $C{\equiv}C$ outer bond with $f = 16.5$ mdyn/Å, in general agreement with theory. The force constants for the two outer bonds of C_6 were reliably determined to be 11.9 and 8.1 mdyn/Å. Larger carbon molecules were formed but not identified.

It has been established that the vapor over graphite at 2500°K contains C, C_2, and C_3 molecules[2-4] which have now been rather thoroughly studied.[5,6] Mass spectrometry[7] has also detected very small quantities

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[1] This research was supported by the Air Force Office of Scientific Research (SRC)-OAR, USAF, Grant No. 68-1588.

[2] W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953); *J. Phys. Chem.*, **59**, 100 (1955).

[3] R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954).

[4] An excellent review of all aspects of the vaporization of carbon has been given by H. B. Palmer and M. Shelef, *Chem. Phys. Carbon*, **4**, 85 (1968).

[5] C_2, E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 84 (1963); C_3, L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *ibid.*, **142**, 45 (1965).