symmetry and to the change of ligand L) that the non-bonding electron pair in each of the chromium and molybdenum complexes and the unpaired electron in each $V(h^5\text{-}C_5H_5)_2L_2$ complex reside in an a_1 orbital of high metal character, primarily $3d_{z^2}$ with only a very small amount of $3d_{x^2-y^2}$ and virtually no $4s$. Each vanadium HOMO also possesses considerable S (or Cl) p orbital character. It is highly significant that the composition of this vanadium HOMO is completely compatible from electron repulsion arguments with the observed decrease of *ca.* 6° in the L–M–L bond angle upon its occupation. Hence, it is evident that the Fenske–Hall MO treatment, even for a one-electron open-shell system, gives excellent agreement with the epr results (*i.e.*, per cent character ratio of $3d_{z^2}/3d_{x^2-y^2}$ = $(0.963)^2/(0.270)^2$ = $12.7/1$ (epr) *vs.* $0.501/0.066$ = $7.7/1$(MO)) with the contributions to the anisotropy in the hyperfine coupling tensor primarily arising from the drastically different per cent character of the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. Details of this work will be presented later together with photoelectron spectroscopic experiments, currently underway, which will provide additional insight concerning the bonding in these species.

Since the submission of this communication, an article by Stewart and Porte[17] reporting the dilute glass epr spectra for several $V(h^5\text{-}C_5H_5)_2L_2$ compounds (L = Cl, SCN, OCN, and CN) has been published. Due to the nature of this type of experiment, the authors have incorrectly assigned the z component of the magnetic tensors to coincide with the C_2-2 axes of these molecules.

The noncoincidence of the **g** and **T** tensors in $V(h^5\text{-}C_5H_5)_2S_5$ is presumed to be at least partially a consequence of the significant deviations of the molecule (of crystallographic site symmetry C_1-1) from C_2-2 symmetry. The orbital character of the unpaired electron was obtained from an analysis of the principal values of the **T** tensor. Since the expressions for the anisotropic part of the hyperfine components are second order in **g** and λ, these parameters do not significantly affect either the magnitude of the anisotropic components of **T** or the subsequent values of a and b.

In order to provide an operational test of the research and resulting conclusions presented here, we have synthesized and determined the crystal structures of the nonisomorphous $V(h^5\text{-}C_5H_4CH_3)_2Cl_2$ and $Ti(h^5\text{-}C_5H_4CH_3)_2Cl_2$ (both of which possess ordered solid-state structures) and have carried out a single-crystal epr analysis of $V(h^5\text{-}C_5H_4CH_3)_2Cl_2$ (of crystallographic C_2-2 site symmetry) diluted in the crystal lattice of $Ti(h^5\text{-}C_5H_4CH_3)_2Cl_2$ (of crystallographic C_s-m site symmetry). The **g** and **T** tensors are coincident for $V(h^5\text{-}C_5H_4CH_3)_2Cl_2$, and the orientation of their principal directions is identical with the orientation of the principal directions of **T** for $V(h^5\text{-}C_5H_5)_2S_5$ shown in Figure 1. The per cent character for the HOMO in $V(h^5\text{-}C_5H_5)_2Cl_2$ agrees remarkably well with that calculated for the methylcyclopentadienyl vanadium analog from its epr data (*i.e.*, per cent character ratio of $3d_{z^2}/3d_{x^2-y^2}$ = $(0.976)^2/(0.218)^2$ = 20.0 (epr) *vs.* $(0.676)/(0.033)$ = $20.5/1$ (MO)). These results thereby provide

(17) C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 722 (1973).

further convincing evidence of our interpretation of the principal values and directions of the hyperfine tensor in $V(h^5\text{-}C_5H_5)_2S_5$ concerning the distribution of the unpaired electron in this d^1 V(IV) species.

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The Chemistry of "Naked" Anions. I. Reactions of the 18-Crown-6 Complex of Potassium Fluoride with Organic Substrates in Aprotic Organic Solvents[1]

Sir:

Fluoride ion, unencumbered by strong solvation forces, should prove to be both a potent nucleophile and base.[2] Solubility problems, however, have hampered studies of fluoride ion in weakly solvating media. The recent reports regarding the ability of crown ethers to complex metal salts and dissolve them in polar and nonpolar, aprotic solvents[3,4] has prompted us to investigate the chemistry of metal fluoride crown complexes. We wish to report the solubilization of potassium fluoride in acetonitrile and benzene containing 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6) (1)[5,6] and the reactions of this solubilized fluoride, which

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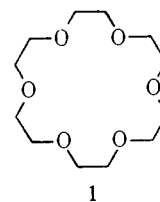
we have termed "naked" fluoride, with a variety of organic substrates. The following reaction types are demonstrated: (1) displacement reactions at sp^3

(1) Presented in part at the First Fall Organic Conference, Cape Cod, Mass., Oct 1, 1973.
(2) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 14–17.
(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970); *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968); C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, **84**, 16 (1972); J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971).
(4) D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, **94**, 4024 (1972).
(5) R. Greene, *Tetrahedron Lett.*, 1793 (1972).
(6) D. J. Cram and G. Gokel, Department of Chemistry, University of California at Los Angeles, private communication.

Table I. Reactions of "Naked" Fluoride with Organic Substrates

Substrate	Solvent	Products[a]	Concentrations (M)		Temp, °C	$t_{1/2}$, hr[b]
			Crown	Substrate		
Benzyl bromide	CH₃CN	Benzyl fluoride	0.19	2.0	83	11.5
1-Bromooctane	CH₃CN	1-Fluorooctane (92%)	0.19	1.16	83	115
		1-Octene (8%)				
	C₆H₆	1-Fluorooctane (92%)	0.68	2.9	90	128
		1-Octene (8%)				
2-Bromooctane	C₆H₆	2-Fluorooctane (32%)	0.50	2.8	90	240
		1- and 2-octenes (68%)				
Bromocyclohexane	CH₃CN	Cyclohexene	0.15	3.61	83	104
2-Chloro-2-methylcyclohexanone	CH₃CN	2-Fluoro-2-methylcyclohexanone (31%)	0.15	3.3	83	20
		2-Methyl-2-cyclohexenone (69%)				
2,4-Dinitrochlorobenzene	CH₃CN	2,4-Dinitrofluorobenzene			25	5
					83	0.12
Acetyl chloride	CH₃CN	Acetyl fluoride	0.14	7.0	25	5.5

[a] In all cases conversion to products was quantitative. All spectral data (nmr, ir, and mass spectral) of the isolated products were consistent with the assigned structures. [b] The time for one-half conversion of starting materials to products is tabulated as an approximate indication of the relative rates of reaction.

hybridized carbon with leaving groups located at primary, secondary, tertiary, and benzylic positions, (2) competing elimination processes, and (3) displacement reactions at sp² hybridized carbon. The data are summarized in Table I. The reaction conditions are relatively mild and the conversions essentially quantitative. Less than 5% reaction takes place in the absence of crown ether under identical conditions covering the same periods of time.

The products of reaction are either fluorides, alkenes, or mixtures of these indicating that "naked" fluoride may act as both a nucleophile or a base. Benzyl bromide reacts rapidly to produce benzyl fluoride.[7] Primary halides give predominantly primary fluorides with only small amounts of alkene whereas secondary halides give exclusively or predominantly alkene products.[8] An interesting reaction illustrating the competition between displacement and elimination processes is the reaction of "naked" fluoride with 2-chloro-2-methylcyclohexanone (2) to produce 2-fluoro-2-methylcyclohexanone (3) and 2-methyl-2-cyclohexenone (4).[9] It has been found that alkyl chlorides react

2   **4**   **3**
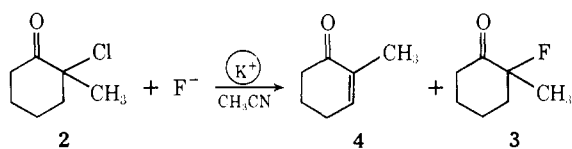
slowly with "naked" fluoride while the corresponding tosylates have reactivity comparable to that of bromides. This observation regarding leaving group abilities is in

line with the tabulation reported by Streitwieser for homogeneous reactions.[10] In addition, reaction appears to be faster in acetonitrile than in benzene. Displacement at sp² hybridized carbon, as illustrated by the reactions of 2,4-dinitrochlorobenzene and acetyl chloride, occur smoothly at room temperature and rapidly at reflux to give 100% conversion to the corresponding fluorides.[11,12]

The reagent is prepared by dissolving 18-Crown-6 in dry acetonitrile[13] or dry benzene and then adding dry potassium fluoride.[14] After the heterogeneous system is stirred for 30 min, the organic substrate is added and the resulting mixture stirred until reaction is complete. It should be emphasized that efficient stirring is important for complete reaction to be attained. This, like the solubilization of KMnO₄ in benzene reported by Sam and Simmons,[4] is an example of solution of an insoluble salt directly in a solvent such as acetonitrile or benzene simply by adding crown ether. Usually a solvent exchange procedure is employed to solubilize the salt.[3] In all cases reported in Table I, the crown is present in catalytic concentrations.

The concentration of naked fluoride in solution at 25° has been determined from analysis of the potassium ion concentration by flame photometry. The results are shown in Table II. It is interesting to note that a plot of the solubility of potassium–crown–fluoride vs. the concentration of crown in solution produces a reasonable straight line passing near the origin. It appears, therefore, that the concentration of solubilized KF is independent of the dielectric constant of the medium.

(7) Benzyl fluoride has been prepared from benzyl bromide by a variety of methods with yields ranging from 30 to 70%: A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," American Chemical Society Monograph No. 155, Reinhold, New York, N. Y., 1962; J. Bernstein, J. S. Roth, and W. T. Miller, Jr., J. Amer. Chem. Soc., 70, 2310 (1948); J. J. Delpuech and C. Beguin, Bull. Soc. Chim. Fr., 791 (1967); J. F. Normant and J. Bernardin, C. R. Acad. Sci., Ser. C, 268, 2352 (1969); E. D. Bergmann and A. M. Cohen, Isr. J. Chem., 8, 925 (1970).

(8) Alkyl fluorides have been prepared in yields ranging from 20 to 50% from alkyl halides and alkyl p-toluenesulfonates using KF in a variety of solvents: F. L. M. Pattison, "Toxic Aliphatic Fluorine Compounds," Elsevier, Amsterdam and New York, 1959; F. L. M. Pattison, R. L. Buchanan, and F. H. Dean, Can. J. Chem., 43, 1700 (1965); F. L. M. Pattison and J. J. Norman, J. Amer. Chem. Soc., 79, 2311 (1957), and references cited therein; F. W. Hoffman, ibid., 70, 2596 (1948); W. F. Edgell and L. Parts, ibid., 77, 4899 (1955).

(9) A 40% conversion of 2 to 4 has been reported using collidine at 145–200° or LiCl in dimethylformamide at 110°: "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963; pp 162–166.

(10) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 29–31.

(11) 2,4-Dinitrofluorobenzene has been prepared in 92% yield by heating the corresponding chloride with KF in the absence of solvent at 190–200° for 7 hr. The same conversion was reported in 51–98% yield using KF, CsF, or RbF at 195° for 2 hr in a variety of solvents: N. N. Vorozhtsov, Jr., and G. G. Yakobson, Zh. Obshch. Khim., 27, 1672 (1957); Chem. Abstr., 52, 2777g (1958); J. Gen. Chem. USSR, 27, 1741 (1957); J. Gen. Chem. USSR, 31, 3459 (1961).

(12) Acetyl fluoride has been prepared by the action of ZnF₂ on acetyl chloride at 50° and by the action of hydrogen fluoride and sodium fluoride on acetic anhydride at 0°: A. L. Henne, Org. React. 2, 61 (1944), and references cited therein.

(13) It has been found that the upper concentration limit of 18-Crown-6 in acetonitrile is approximately 0.2 M at room temperature while concentrations as high as 1.5 M have been easily achieved in benzene.

(14) Commercial anhydrous KF was dried in an oven at 120° at atmospheric pressure for 12 hr. A mole ratio of potassium fluoride to organic substrate of 2:1 was used in all cases.

Table II. Solubility of Potassium Fluoride in Crown Ether Solution at 25°

Solvent	[18-Crown-6], M	[KF], M
Benzene	1.01	5.2×10^{-2}
	0.34	1.4×10^{-2}
Acetonitrile	0.16	3.5×10^{-3}

In conclusion, it has been shown (1) that the 18-Crown-6 is an effective agent for the solubilization of KF in polar and nonpolar, aprotic organic solvents, (2) that this solubilized fluoride ("naked" fluoride) is both a potent nucleophile and base, and (3) that the "naked" fluoride reagent provides a facile and efficient means of obtaining organic fluorine compounds in high yield.

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Crown Ether Chemistry. Substitution Reactions of Potassium Halide and Potassium Hydroxide Complexes of Dicyclohexyl-18-crown-6[1]

Sir:

The crown ethers form complexes with alkali and other metal salts which sometimes provide increased salt solubility and increased anion reactivity in aprotic organic solvents.[2-5] We have now observed (1) enhanced reactivity of the KBr and KI complexes 1 and 2 in acetone in nucleophilic substitution and elimination reactions and (2) a surprisingly facile, nucleophilic aromatic substitution reaction of the previously reported[2] KOH complex 3 in aromatic hydrocarbons.
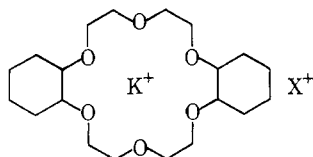
1, $X^- = Br^-$
2, $X^- = I^-$
3, $X^- = OH^-$; OCH_3^-

Potassium bromide is essentially insoluble in refluxing anhydrous acetone, even when an equimolar amount of dicyclohexyl-18-crown-6 is present. Pure crystalline 1 was prepared by Pedersen's method[2] using methanol to solubilize the KBr and crown ether. Dissolution of 1 in acetone then gives 0.06–0.07 M solutions. Complex 2 (0.16 M in acetone) and 3 (0.3 M in toluene) were prepared similarly.[6]

(1) Presented in part at the First Fall Organic Conference, Cape Cod, Mass., Oct 1973.

(2) (a) C. J. Pedersen, *J. Amer. Chem. Soc.*, **92**, 391 (1970); *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968); (b) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, **84**, 16 (1972).

(3) D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, **94**, 4024 (1972).

(4) (a) M. Svoboda, J. Hapala, and J. Zavada, *Tetrahedron Lett.*, 265 (1972); (b) R. A. Bartsch and K. E. Wiegers, *ibid.*, 3819 (1972).

(5) C. L. Liotta, Abstracts of First Fall Organic Conference, Cape Cod, Mass., Oct 1973, Abstract No. 5.

(6) The KCl complex was formed in methanol; however, attempts to prepare crystalline KCl and KF complexes or acetone solutions of these complexes were unsuccessful.

Reaction of the pure crystalline complexes 1 and 2[7] with *n*-butyl brosylate in acetone at 25.0° gave clean second-order nucleophilic substitution kinetics.[8] Because of the insolubility of KBr in acetone, little or no reaction occurs in the absence of crown complexation. It was of interest to determine the type of reactive halide (ion or ion pair) in these S_N2 reactions and to compare their reactivity with other halide salts. From a comparison of the observed rate constants, k_2 (Table I), the

Table I. Kinetic Data for Reaction of 0.04 M Salts with *n*-Butyl Brosylate in Acetone at 25.0°

$$MX + n\text{-}BuOBs \longrightarrow n\text{-}BuX + M^+OBs^-$$

MX[d]	$10^3 k_2$, l. mol^{-1} sec^{-1} [a]	α	$10^3 k_2'$, l. mol^{-1}sec^{-1} [b]
CE–KCl (isomer A)			
CE–KBr (isomer A)	9.72	0.75–0.80[c]	
CE–KI (isomer A)	2.08	0.58–1.0[c]	
CE–KI (isomer B)	2.32		
Bu$_4$NCl	33.5	0.58	58
Bu$_4$NBr	9.09	0.70	13
Bu$_4$NI	1.68	0.84	2.0
LiCl	0.493	0.0097	51
LiBr	2.81	0.23	12
LiI	2.97	0.83	3.6

[a] Duplicate runs in good agreement were obtained. We observed the same rate constants for Bu$_4$NX and LiX as Winstein.[8] [b] Rate constants corrected for ion dissociation; $k_2' = k_2/\alpha$. [c] Calculated degree of dissociation using k_2' of Bu$_4$NX and LiX; $\alpha_{CE} = k_{2CE}/k_2'$. α for Bu$_4$NX and LiX were determined by conductance.[8] [d] CE = dicyclohexyl-18-crown-6.

crown complex halides show a greater nucleophilic reactivity than the predominantly dissociated *n*-Bu$_4$N$^+$ halides and the mostly undissociated LiBr.[8] This increased reactivity is noteworthy since the *n*-Bu$_4$N$^+$ halides are regarded as reactive halides in organic solvents. We believe this reactivity can be attributed to significant ion dissociation. Winstein[8] and Weaver[9] have provided good evidence that the numerical values and trends in ordering of observed rate constants similar to those we observed for the crown complexes are best ascribed to reactive dissociated halide ions rather than ion pairs.[10] Also, Frensdorff[2b,11] has shown that complexation of KCl with dicyclohexyl-18-crown-6 in CH_3OH–$CHCl_3$ increases dissociation of ion pairs as determined by increased conductance. We conclude that crown complexation of potassium ions leads not only to increased halide reactivity but also to greater ion dissociation than *n*-Bu$_4$N$^+$. From the data in Table I, the degree of dissociation (α) at 4×10^{-2} M

(7) Two cis-ring juncture isomers of dicyclohexyl-18-crown-6 are obtained from hydrogenation of dibenzo-18-crown-6. Isomer A (mp 61–62°) is the syn isomer and isomer B is the anti isomer.[7b] Satisfactory analyses were obtained for all complexes: isomer A–KBr mp 114–115°, –KI mp 184–185°; isomer B–KBr mp 100–102°, –KI mp 120–121°. (b) D. E. Fenton, M. Mercer, and M. R. Truter, *Biochem. Biophys. Res. Commun.*, **48**, 10 (1972).

(8) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, **9**, 24 (1960). Halide ions were assayed by potentiometric titration and the Volhard method. Infinity titer analyses showed only *n*-butyl halide products.

(9) W. M. Weaver and J. D. Hutchinson, *J. Amer. Chem. Soc.*, **86**, 261 (1964).

(10) The contribution of ion-pair reactivity is now known. To accommodate the data in Table I in terms of reactive ion pairs, it is difficult to rationalize that both the crown complexed and tetraalkylammonium halide ion pairs must be much more reactive than dissociated halide ions, whereas under identical kinetic conditions lithium halide ion pairs must be much less reactive than dissociated halide ions.

(11) H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 4684 (1971).