It is interesting that the correlations in Figures 1 and 2 extend to a base as large and basic as HMPA. First it is surprising that HMPA does not appear to suffer from a severe steric barrier in complexing the uranyl ion. An X-ray structural analysis of $UO_2(hfacac)_2HMPA$ has recently been done, and it in fact shows a very close approach of the methyl groups to the CF_3 groups of the anion.[9] Second, HMPA is known to be able to coordinate the uranyl ion to form a complex in which four HMPA molecules are tightly bound and the counterions are removed from the inner coordination sphere.[10] We believe similar species can form when HMPA reacts with the $UO_2[(CF_3CO)_2CH]_2$ system, but they do not appear to exert a strong effect on the equilibrium measurements of 1:1 solutions with the uranyl ion. Why the size and tendency toward multiple coordination of the base does not disturb the measured correlations is not immediately evident and is being studied further.

In summary the chelated uranyl ion has been found to bind to oxygenated bases through a strongly electrostatic interaction which increases with the general basicity of these compounds as shown by the way they bind to other relatively hard Lewis acids. Equilibrium measurements in chloroform afford a convenient basicity scale with which to assess the overall nucleophilicity of both protic and aprotic bases.

Registry No. 1, 69244-67-3; $UO_2[(CF_3CO)_2CH]_2 \cdot Me_2SO$, 75172-91-7; $UO_2[(CF_3CO)_2CH]_2$, 67316-66-9; cyclobutanone, 1191-95-3; 4-methyl-1,3-dioxolan-2-one, 108-32-7; $(C_2H_5)_2O$, 60-29-7; 1,4-dioxane, 123-91-1; CH_3COCH_3, 67-64-1; tetrahydro-3-methylthiophene 1,1-dioxide, 872-93-5; H_2O, 7732-18-5; cyclopentanone, 120-92-3; tetrahydro-2*H*-pyran-2-one, 542-28-9; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; oxetane, 503-30-0; $(C_4H_9)_2SO$, 2168-93-6; $(CH_3)_2SO$, 67-68-5; $CO[N(CH_3)_2]_2$, 632-22-4; $(MeO)_3P{=}O$, 512-56-1; $HCO[N(CH_3)_2]$, 68-12-2; $(Me)_3P{=}O$, 676-96-0; pyridine 1-oxide, 694-59-7; $Et_3P{=}O$, 597-50-2; $[(CH_3)_2N]_3P{=}O$, 680-31-9; $(CH_3O)_2SO_2$, 77-78-1; CF_3CH_2OH, 75-89-8; aniline, 62-53-3; pyridine, 110-86-1; acetonitrile, 75-05-8; THF, 109-99-9; $(CH_3)_3Al$, 75-24-1; $(C_2H_5)_3Al$, 97-93-8; $(C_2H_5)_3Ga$, 1115-99-7; $Cu[(CF_3Co)_2CH]_2$, 14781-45-4; $(CH_3)_3B$, 593-90-8; Cl_5Sb, 7647-18-9.

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[9] G. M. Kramer, E. T. Maas, Jr., D. A. Rapp, and J. C. Scanlon, manuscript in preparation.

[10] L. R. Nassimbeni and A. L. Rodgers, *Cryst. Struct. Commun.*, **5**, 301 (1976).

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Exxon Research and Engineering Company, Linden, New Jersey 07036

Equilibrium Studies with the Uranyl Ion: Nitrogen Bases and Uranyl Hexafluoroacetylacetonates

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Displacement equilibria between the THF adduct of uranyl hexafluoroacetylacetonate and nitrogen-containing bases have been measured by NMR. Experiments have been conducted in chloroform and 2,2,2-trifluoroethanol. The basicity increases markedly from pyrrole and nitriles (which are weaker bases than THF) to amines which are much stronger. Steric effects appear to be important only when the amine is very large.

The chelated uranyl ion in $UO_2[(CF_3CO)_2CH]_2$ has been shown to behave as a relatively hard Lewis acid in its reactions with oxygenated bases.[1] Displacement equilibria with these bases have been conveniently studied by proton magnetic resonance, and a basicity order has been established.

This paper reports on the extension of the basicity scale to cover a wide range of nitrogen bases. The base strength of these compounds is tabulated relative to THF for the equilibria

$$B + UO_2[(CF_3CO)_2CH]_2 \cdot THF \xrightleftharpoons[DCCl_3]{} THF + UO_2[(CF_3CO)_2CH]_2 \cdot B \quad (1)$$

Experimental Section

The equilibria of relatively weak N bases were assessed from direct measurements of the ^1H NMR shift of the α-CH_2 group of tetrahydrofuran as before.[1] An overlapping procedure using the Me_2SO adduct of the uranyl chelate was again used to evaluate stronger bases, but in many cases the N-base complexes tended to precipitate from chloroform and equilibria could not be easily measured. So that relative basicity of these bases could be evaluated, similar equilibrium studies were made in 2,2,2-trifluoroethanol. Preliminary measurements had indicated that a direct proportionality exists between measurements in this weakly nucleophilic solvent and those in $DCCl_3$, despite the fact that the alcohol is a stronger proton donor. It was assumed that this proportionality exists to the extremes of the basicity scale examined in this study so that basicity values for strong nitrogen bases in chloroform could be estimated.

Results and Discussion

Table I lists the derived values of free energy change for base exchange and orders the nitrogen bases according to their nucleophilicity toward the chelated uranyl ion. These values are integrated in Table II with those observed for oxygen donor bases.

A basicity scale of nitrogen-containing, organic Lewis bases toward the $UO_2[(CF_3CO)_2CH]_2$ moiety was constructed from solution equilibrium data in $DCCl_3$. By use of CF_3CH_2OH as a solvent, this scale was extended to include a variety of primary, secondary, and tertiary amines which form insoluble species with the uranyl moiety in chloroform. In this less nucleophilic solvent, it was necessary to employ $UO_2[(CF_3CO)_2CH]_2 \cdot Me_2SO$ as the reference material whereas $UO_2[(CF_3CO)_2CH]_2 \cdot THF$ had been employed in $DCCl_3$. The equilibria between $UO_2[(CF_3CO)_2CH]_2 \cdot Me_2SO$ and 2,6-dimethoxypyridine, aniline, pyridine, trimethyl phosphite, trimethyl phosphate, and pyridine *N*-oxide were studied in both solvents in order to correlate the basicity scales of the two solvents. The equilibria with the Me_2SO complex in $DCCl_3$ have been shown previously to be related to those of the analogous THF complex by the expression

$$(\Delta G^\circ)_{THF} = (\Delta G^\circ)_{Me_2SO} - 2.2 \text{ kcal/mol} \quad (2)$$

Calculated equilibria of the THF complex in $DCCl_3$ is plotted vs. equilibria of the Me_2SO complex in CF_3CH_2OH in Figure 1, and an extrapolation is made to include several amines

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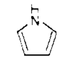
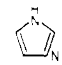
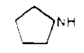
[1] G. M. Kramer, E. T. Maas, Jr., and M. B. Dines, *Inorg. Chem.*, in press.

0020-1669/81/1320-1418$01.25/0

Table I. Base Strength of N Compounds

$UO_2[(CF_3CO)_2CH]_2 \cdot THF + B \rightleftharpoons UO_2[(CF_3CO)_2CH]_2 \cdot B + THF$

base	$\Delta G°$, kcal/mol	
	$DCCl_3$	CF_3CH_2OH[a]
Observed Values		
	4.6	
$CH=CHC\equiv N$	3.8	
$C_6H_5C\equiv N$	3.8	
$CH_3C\equiv N$	3.5	
2,6-$(CH_3O)_2C_5H_3N$	2.9	1.6
$C_6H_5NH_2$	2.1	1.5
2,6-$(CH_3)_2C_5H_3N$	1.35	
$C_6H_5N(CH_3)_2$	1.0	
2-$CH_3C_5H_4N$	−0.05	
C_5H_5N	−1.2	0.2
Estimated Values		
CH_3NH_2	−2.4	0.0
2,6-$(CH_3)_2$-c-C_5H_8NH	−4.0	−0.5
$(C_3H_7)_3N$	−4.6	−0.7
c-$C_3H_5NH_2$	−5.9	−1.1
	−6.2	−1.2
	−8.1	−1.8
$(C_2H_5)_3N$	−8.7	−2.0
$NH_2CH_2CH_2NH_2$	−12.9	−3.3

[a] This column is for equilibria with the uranyl-Me_2SO complex.

measured in the fluorinated alcohol. At least-squares fit of the data indicates that

$$[(\Delta G°)_{THF}]_{DCCl_3} = [3.18(\Delta G°)_{Me_2SO}]_{CF_3CH_2OH} - 2.37 \text{ kcal/mol} \quad (3)$$

The data in Figure 1 indicate an important solvent effect upon equilibrium 1. Thus, the relative basicity of a series of bases appears to change less in trifluoroethanol than in chloroform. The phenomenon is primarily attributed to hydrogen bonding to the free bases, with the stronger bases interacting relatively more strongly with the solvent than the weaker bases. In less polar and more aprotic media, this interaction should be minimized, and the solution equilibria should more closely mimic those in the gas phase.

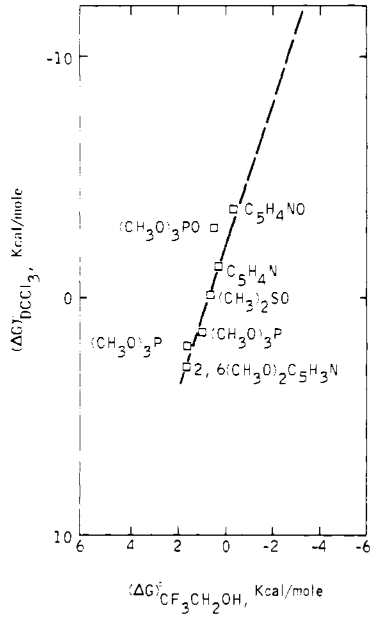


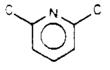
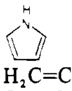
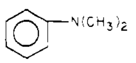
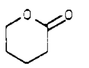
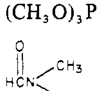
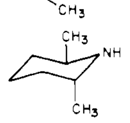
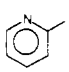
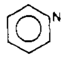
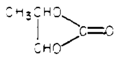
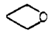
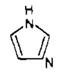
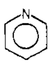
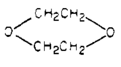
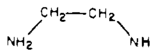
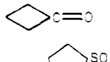
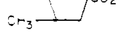
Figure 1. Comparison of $DCCl_3$ and CF_3CH_2OH as solvents for $UO_2[(CF_3CO)_2CH]_2 \cdot THF + B$ equilibria.

The data in Table II indicate that pyrrole and nitriles are weak bases toward the uranyl ion and are even weaker than 2,6-dimethylpyridine (whose steric requirements often prevent its bonding to Lewis acids). Both 2,6-dimethylpyridine and 2-methylpyridine are weaker than THF, while pyridine is a better nucleophile. The aliphatic amines and aziridine generally are stronger bases than the oxygenated bases.

The data are qualitatively in accord with H. C. Brown's studies of molecular addition compounds between amines and pyridine derivatives and Lewis acids[2] and can be examined to

Table II. Relative Base Strength in $DCCl_3$

$UO_2[(CF_3CO)_2CH]_2 \cdot THF + B \rightleftharpoons UO_2[(CF_3CO)_2CH]_2 \cdot B + THF$

base	$\Delta G°$, kcal/mol	base	$\Delta G°$, kcal/mol	base	$\Delta G°$, kcal/mol
CS_2	5.1		1.8	$(C_4H_9)_2SO$	−1.6
$(CH_3O)_2SO_2$	4.8		1.35	CH_3NH_2	−2.4
	4.6	H_2O	1.3	$(CH_3)_2SO$	−2.2
$H_2C=CHC\equiv N$	3.8		1.0	$(CH_3O)_3P=O$	−2.8
$C_6H_5C\equiv N$	3.8		1.0		−2.9
$CH_3C\equiv N$	3.5	CH_3OH	0.5		−4.0
CF_3CH_2OH	3.5		−0.05		−3.6
2,6-$(CH_3O)_2C_5H_3N$[a]	2.9		0.0	$(C_3H_7)_3N$	−4.6
c-$C_4H_6=O$	2.9	C_2H_5OH	−0.2	c-$C_3H_5NH_2$	−5.9
	2.7		−0.5		−6.2
$(C_2H_5)_2O$	2.2		−1.2		−8.1
$C_6H_5NH_2$	2.1			$(C_2H_5)_3N$	−8.7
	2.0				−12.9
	1.9				
	1.9				

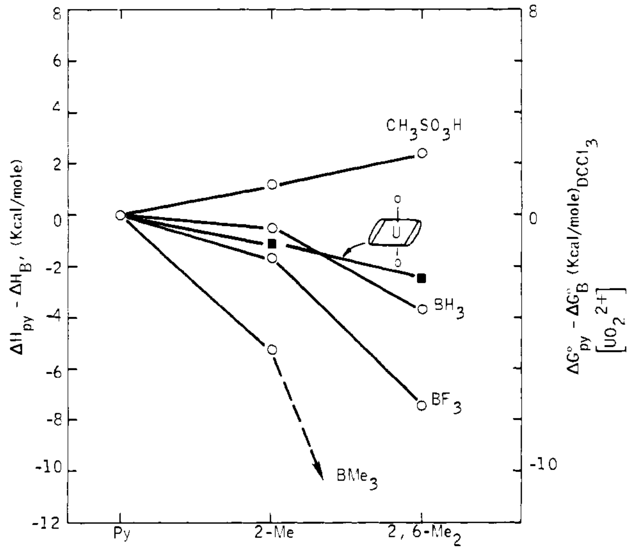


Figure 2. Relative strengths of pyridine, 2-picoline, and 2,5-lutidine with reference acids of increasing steric requirements. $UO_2[(CF_3CO)_2CH]_2$ has small steric requirements.

evaluate the steric requirements of the chelated uranyl ion.

Figure 2 shows Brown's data on the relative heat of dissociation of pyridine, 2-methylpyridine, and 2,6-dimethylpyridine with different acids. Although these compounds show increased basicity toward the proton donor CH_3SO_3H, they bond progressively less well with BH_3, BF_3, and $B(CH_3)_3$. These results are attributed to increasingly severe steric interactions. Protonation has very small steric requirements, while complexing with trimethylboron has a very large requirement.

Added to Figure 2 is the relative free energy associated with the binding of pyridine derivatives to $UO_2[(CF_3CO)_2CH]_2$. The uranyl ion clearly has a steric demand, since 2,6-dimethylpyridine binds less strongly than pyridine, but its requirements appear to be minimal (even less than BH_3). The reason for this behavior can be suggested from X-ray studies of the tetrahydrofuran,[3] trimethyl phosphate,[4] and hexamethylphosphoramide[5] adducts of this uranyl chelate. They all show that the Lewis base bonds via its strongly polarized oxygen atom, which occupies the fifth position of a pentagonal ring surrounding the uranyl ion. The oxygen atoms of the anion occupy the other sites and the five oxygen atoms are nearly equidistant from each other (about 2.8 ± 0.1 Å in the HMPA complex). For clarity the structure of the THF complex[3] is reproduced in Figure 3. In this configuration the CF_3 groups proximal to the base have been pushed back and spread, while the remote CF_3 groups are slightly crowded. The important point is that there appears to be little barrier to displacing the anions about the pentagonal ring to accommodate the base. This is apparent since HMPA, which is significantly larger than trimethyl phosphate or tetrahydrofuran, actually approaches the uranium atom a little more closely, the U–O(base) distances being 2.28, 2.31, and 2.35 Å in the respective compounds.

The behavior of methylamine and the stronger bases in Table I may be rationalized qualitatively on electronic and steric grounds. Secondary and tertiary amines are normally stronger bases than primary amines, an effect usually ascribed to larger polarizability of the alkyl groups,[6] and this is seen here. However, when the base becomes very large, steric crowding becomes important. In the case of the uranyl compound, this is manifested by a decreased bonding of tripropylamine, compared to that of triethylamine, $\Delta G^\circ = -4.6$ v. -8.7 kcal/mol. A steric effect is also evident in the bonding of pyrrolidine and 2,6-dimethylpiperidine, for which the ΔG° values are -8.1 and -4.0 kcal/mol.

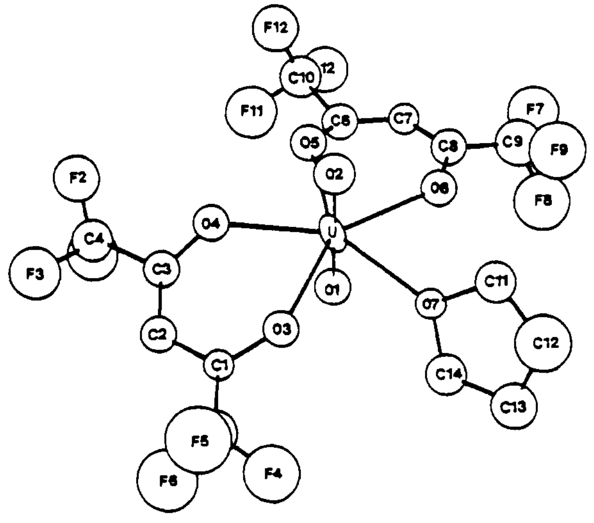


Figure 3. Structure of $UO_2[(CF_3CO)_2CH]_2 \cdot THF$.

Conclusion

The overall binding of N bases toward the uranyl ion is seen to vary widely. The weakest bases (such as the nitriles) bond about the same as poorly nucleophilic oxygen compounds (e.g., trifluoroethanol). However, the unhindered secondary and tertiary amines appear to bond about 10–15 kcal/mol more strongly than the nitriles. These are values in solution and are expected to be less than in the gas phase. One reason is that the dielectric constant of the solvent will preferentially reduce the attractive potential or ion–dipole interaction between the uranyl ion and a strongly nucleophilic base more than it will the interaction with a poorer nucleophile. The interaction between a 6+ uranium center and oxygen and nitrogen bases is expected to be of the hard acid–hard base variety. It would be interesting to compare the measured equilibria with the corresponding soft sulfur and phosphorus bases, and this is being done. A composite of the equilibria with both oxygen and nitrogen bases as noted above is provided in Table II.

Registry No. $UO_2[(CF_3CO)_2CH]_2 \cdot THF$, 69244-67-3; $(CH_3)_2SO$, 67-68-5; 1*H*-pyrrole, 109-97-7; $CH_2{=}CHC{\equiv}N$, 107-13-1; $C_6H_5C{\equiv}N$, 100-47-0; $CH_3C{\equiv}N$, 75-05-8; 2,6-$(CH_3O)_2C_5H_3N$, 6231-18-1; $C_6H_5NH_2$, 62-53-3; 2,6-$(CH_3)_2C_5H_3N$, 108-48-5; $C_6H_5N(CH_3)_2$, 121-69-7; 2-$CH_3C_5H_4N$, 109-06-8; C_5H_5N, 110-86-1; CH_3NH_2, 74-89-5; 2,6-$(CH_3)_2$-c-C_5H_8NH, 504-03-0; $(C_3H_7)_3N$, 102-69-2; c-$C_3H_5NH_2$, 765-30-0; 1*H*-imidazole, 288-32-4; pyrrolidine, 123-75-1; $(C_2H_5)_3N$, 121-44-8; $NH_2CH_2CH_2NH_2$, 107-15-3; CS_2, 75-15-0; $(CH_3O)_2SO_2$, 616-42-2; CF_3CH_2OH, 75-89-8; c-$C_4H_6{=}O$, 1191-95-3; $OCH_2CH(CH_3)OC(O)$, 108-32-7; $(C_2H_5)_2O$, 60-29-7; $OCH_2CH_2OCH_2CH_2$, 123-91-1; $CH_2CH(CH_3)CH_2CH_2S(O)_2$, 872-93-5; cyclopentanone, 120-92-3; H_2O, 7732-18-5; $OCH_2CH_2CH_2CH_2C(O)$, 542-28-9; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; $OCH_2CH_2CH_2$, 503-30-0; $(C_4H_9)_2SO$, 2168-93-6; $(CH_3O)_3P$, 121-45-9; $(CH_3O)_3P{=}O$, 512-56-1; $HC(O)N(CH_3)_2$, 68-12-2; C_5H_5NO, 694-59-7.

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(2) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, NY, 1972, Chapter V.

(3) G. M. Kramer, M. B. Dines, R. B. Hall, A. Kaldor, A. R. Jacobsen, and J. C. Scanlon, *Inorg. Chem.*, **19**, 1340 (1980).

(4) J. C. Taylor and A. B. Waugh, *J. Chem. Soc., Dalton Trans.*, 1630 (1977).

(5) G. M. Kramer, E. T. Maas, Jr., D. A. Rapp, and J. C. Scanlon, manuscript in preparation.

(6) J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 3914 (1971).