(w, SF_5O), and 610 (s, δ SF_5O). The OH stretch and OOH bending are very close to those observed for CF_3OOH.[1,2] The three strong absorptions below 1000 cm^{-1} are typical for SF_5O derivatives.[7-10] The Raman spectrum of F_5SOOH shows a very intense scattering at 735 cm^{-1} which, by analogy to fluorocarbon peroxides, can tentatively be assigned to the O–O stretch.[11]

The ^{19}F nmr of F_5SOOH at 94.1 MHz shows 21 lines which are nearly identical in intensity with the calculated spectrum for an A_4B system with $J/\delta = 0.25$.[12] The ^1H nmr shows a single, somewhat broadened, line at $\delta = -10.03$. No H–F coupling is observed and the broad ^1H nmr signal is due to intermolecular exchange of H on oxygen. A detailed analysis of the ^{19}F nmr spectrum is in progress.

The mass spectrum of SF_5OOH at a variety of ionization potentials and source temperatures gives F_3SO^+ (*m/e* 105) as the most intense ion followed by FSO^+ (67), F_2SO^+ (86), F_3S^+ (89), and F_2S^+ (70). In addition, an intense ion at *m/e* 32 is observed corresponding to O_2^+, providing support for the decomposition of the compound to form O_2 and the presence of an O–O grouping. No parent ion above background could be observed and heavier ions such as F_5SOO^+ and F_5SO^+ were also absent. The observed mass fragmentation is very similar to certain other SF_5OX derivatives, especially where X is Cl or NF_2.[8,9] However, it is also similar to that of SOF_4[10] and the possibility that the spectrum is due entirely to the decomposition products of F_5SOOH cannot be ruled out.

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Determination of Carbonium Ion Stabilities by Ion Cyclotron Resonance Spectroscopy

Sir:

Substituent effects on carbonium ion stabilities have been used extensively to explain patterns of chemical reactivity.[1] Using trapped ion cyclotron resonance techniques[2-7] it should in principle be possible to determine relative carbonium ion stabilities from studies of hydride transfer equilibria (eq 1) in the gas phase. Consistent with previous results,[8] we have found the forward and reverse rate constants for reaction 1 to be slow for interesting pairs of carbonium ions (*e.g.*, *tert*-butyl and isopentyl) with equilibrium being established only after several hundred collisions.[9] *We wish to report an alternate and more successful approach for the determination of carbonium ion stabilities involving study of the halide transfer equilibria generalized in eq 2.* Chosen to exemplify these studies is a consideration of the relative stabilities of the fluoromethyl cation ($CH_nF_{3-n}^+$, $n = 0$–3). The effects of fluorine substituents on carbonium ion stabilities are of particular interest since they exhibit ambiguous behavior.[10,11] While dative π bonding from fluorine p–π orbitals to the empty carbon p orbital is a stabilizing effect, the large electronegativity of fluorine relative to hydrogen serves to destabilize positive charge on carbon.

$$R_1^+ + R_2H \rightleftharpoons R_2^+ + R_1H \qquad (1)$$

$$R_1^+ + R_2X \rightleftharpoons [R_1\overset{+}{X}R_2]^* \rightleftharpoons R_2^+ + R_1X \qquad (2)$$

Both the occurrence of halide transfer processes and the intermediacy of halonium ions in the reactions of carbonium ions with alkyl halides have been documented in continuing studies in our laboratory.[12,13] For example, the major fragment ions derived from methylene fluoride are CH_2F^+ and CHF_2^+. Reaction 3 accounts for the disappearance of CHF_2^+ at higher pressures or long reaction times, the product CH_2F^+ being unreactive with CH_2F_2.[13] Similarly, in the case of fluoroform, the fragment ion CF_3^+ reacts to generate CHF_2^+, which is unreactive with CHF_3.[13] Hence, in a mixture of CH_2F_2 with CHF_3, reaction 3 can proceed reversibly. This conjecture is confirmed by the data shown in Figure 1. In Figure 1a the relative abundances of CH_2F^+ and CHF_2^+ are observed not to vary significantly with time beyond 100 msec.[3] From the relative ion abundances and known neutral concentrations, an equilibrium constant $K = 0.65$ is derived for reaction 3. To check that equilibrium is established, a *time delay ion ejection technique* is used. In the trapped ion timing sequence an irradiating radiofrequency field is switched on at 100 msec (Figure 1b) and used to continuously remove CH_2F^+ in a time short compared to the time between collisions. Thus reaction 3 can proceed only to the right, causing the subsequent decay of CHF_2^+. From an analysis of the resulting kinetic data, the forward ($k_f = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}) and reverse ($k_r = 2.2 \times 10^{-10}$cm^3 molecule^{-1} sec^{-1}) rate

$$CHF_2^+ + CH_2F_2 \longrightarrow CH_2F^+ + CHF_3 \qquad (3)$$

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Table I. Thermochemical Properties Related to Fluoromethyl Cation Stabilities[a]

R	$\Delta H_f(R)$[b]	$\Delta H_f(RH)$[b]	$\Delta H_f(RF)$[b,c]	IP(R)	$\Delta H_f(R^+)$	$D(R^+–H^-)$[j]	$D(R^+–F^-)$[k]
CH_3	34.0	−17.89	−55.9	9.84[e]	260.9[d]	312.2	255.5
CH_2F	−4.9[d]	−55.9	−108.1	8.90[f]	200.3[h]	289.6	247.1
CHF_2	−59.2	−108.1	−166.3	8.74[d]	142.4[i]	283.9	247.4
CF_3	−112.2	−166.3	−223.0	9.17[g]	99.3[d]	299.0	260.0

[a] All thermochemical data in kcal/mol except ionization potentials which are given in eV. [b] J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3**, 427 (1971). [c] J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968). [d] Calculated from $IP(R) = \Delta H_f(R^+) - \Delta H_f(R)$. [e] G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956). [f] F. P. Lossing, *Bull. Soc. Chim. Belg.*, **81**, 125 (1972). [g] T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, **51**, 3531 (1969). [h] M. Krauss, J. A. Walker, and V. H. Diebler, *J. Res. Nat. Bur. Stand., Sect. A*, **72**, 281 (1968). [i] Calculated from the ΔH value determined for reaction 3 (see text). [j] Calculated from $D(R^+–H^-) = \Delta H_f(R^+) + \Delta H_f(H^-) - \Delta H_f(RH)$. [k] Calculated from $D(R^+–F^-) = \Delta H_f(R^+) + \Delta H_f(F^-) - \Delta H_f(RF)$.

constants have been independently obtained for reaction 3. The calculated equilibrium constant $K = k_f/k_r = 0.64$ is in excellent agreement with that obtained above. This equilibrium constant was examined as a function of electron energy from 13 to 70 eV and was found to be invariant even though the fragmentation patterns of both neutrals change markedly and the internal energies of the fragments are likely to vary considerably.

From these data the free-energy change $\Delta G°_{298} = 0.25$ kcal/mol may be calculated for reaction 3. The entropy change $\Delta S°_{298} = -1.86$ eu is estimated using the standard entropy data of Benson[14] for the neutral molecules and calculating the entropies of the ions assuming the geometry obtained by Baird and Datta,[15] giving $\Delta H°_{298} = -0.3$ kcal/mol. The present data in conjunction with available literature data permit construction of Table I for the properties of fluoromethyl cations. For a reference point we have *arbitrarily* chosen the determination of the photoionization threshold for the production of CH_2F^+ from CH_3F which gives $\Delta H_f(CH_2F^+) = 200.3$ kcal/mol.[16] Combining this value with $\Delta H = -0.3$ kcal/mol for reaction 3 gives $\Delta H_f(CHF_2^+) = 142.4$ kcal/mol. This in is good agreement with the value $\Delta H_f(CHF_2^+) = 142.1$ kcal/mol derived from Lossing's study of the fragmentation processes in CH_2F_2 using monoenergetic electron impact techniques.[17] There are uncertainties on the order of ±2 kcal/mol in many of the data in Table I. *It is to be emphasized, however, that the methodology developed in the present study can yield differences in fluoride affinities accurate to ±0.1 kcal/mol.*

Several criteria may be used to judge the effects of fluorine substituents on carbonium ion stabilities. These include (1) the effect of successive fluorine substitutions on ionic heats of formation; (2) the ionizaton potentials of the corresponding radicals; (3) relative hydride affinities ($R^+–H^-$ heterolytic bond dissociation energies); and (4) relative fluoride affinities ($R^+–F^-$ heterolytic bond dissociation energies). A much smaller decrease (20 kcal/mol less) in ionic heat of formation is observed in proceeding from CHF_2^+ to CF_3^+ than from CH_3^+ to CH_2F^+ and CH_2F^+ to CHF_2^+. Relative ionization potentials of the radicals decrease in the same order, $CH_3 > CF_3 > CH_2F > CHF_2$, as the hydride affinities of the corresponding carbonium ions. Relative fluoride affinities decrease in a somewhat different order, $CF_3^+ > CH_3^+ > CHF_2^+ \cong CH_2F^+$. Thus, with the exception of the latter,[18] a reasonably consistent picture of the effects of fluorine substituents on carbonium ion stability emerges for the data in Table I. The general effect of fluorine is to stabilize the carbonium ion relative to hydrogen. Dative π bonding is apparently most significant in CH_2F^+ relative to CH_3^+ and to a lesser extent in CHF_2^+ and CF_3^+ relative to CH_2F^+. Destabilization of the carbonium ion by electron withdrawal increases with increasing fluorine substitution.

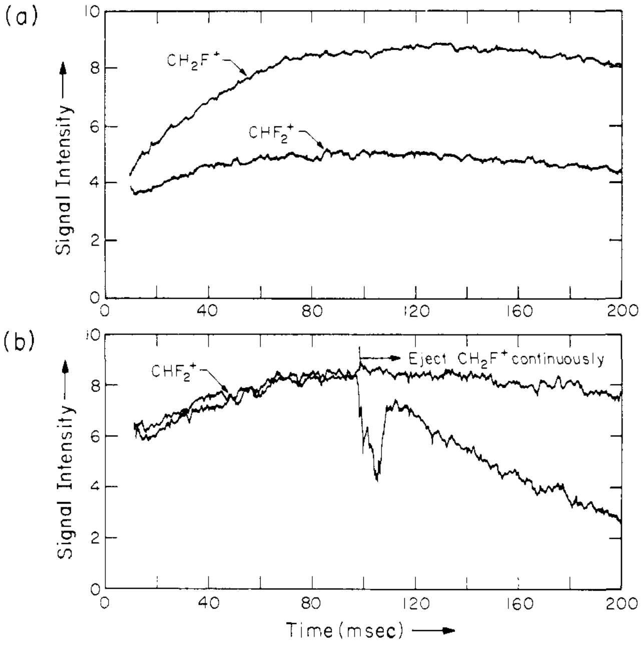

Figure 1. (a) Variation with time of CH_2F^+ and CHF_2^+ ion abundances in a 4.5:1 mixture of CH_2F_2 and CHF_3. Other conditions are 10-msec 70-eV electron beam pulse, total pressure 3.15×10^{-6} Torr. Initial buildup of CH_2F^+ and CHF_2^+ is due to reaction of CF_3^+ (decay not shown). (b) Repeat of CHF_2^+ scan with and without continuous ejection of CHF_2^+ after 100 msec. The anomalous feature in the CHF_2^+ decay curve results from transients generated by turning on the irradiating oscillator in the timing sequence.

These studies have general implications and are being continued to determine the quantitative effect of a wide variety of substituents on carbonium ion stabilities.[19]

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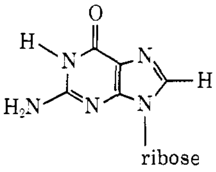
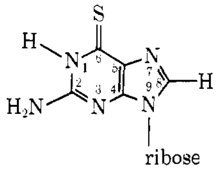
Metal Binding by Thionucleosides

Sir:

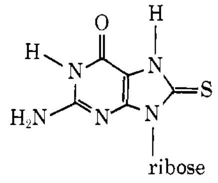
Metal ions and complexes are potentially powerful tools for studying the structure and base sequence of polynucleotides.[1,2] Since naturally occurring polynucleotides have many available binding sites,[3] it appeared useful to investigate the interaction of metals with less common, modified nucleosides, especially thiolated nucleosides. By exploiting the "class b"[4] (or "soft"[5]) nature of the sulfur donor atom, selective and quantitative metal binding was anticipated. In this preliminary report we present equilibrium constants for metal–thionucleoside binding, the synthesis and structure determination of a metal-mercaptopurine complex, and evidence for the metalation and demetalation of a 4-thioU residue, effected during the denaturation and renaturation, respectively, of *E. coli* tRNA^{Val}.



1,G



2, 6-thioG



3,8-thioG

Using nmr, Kan and Li[6] had determined the equilibrium constant, K_1 = 5.9 l./mol, for the binding of mercuric chloride to guanosine (**1**) in DMSO. A similar study in our laboratory with 6-thioguanosine (**2**) indicates the formation of species with a 6-thioG:$HgCl_2$ ratio greater than unity. Assuming a 2:1 complex, the lower limit for the 6-thioG binding constant is 50 times greater than the constant for guanosine.

The binding of sodium *p*-hydroxymercuribenzoate (PHMB) to thionucleosides **2** and **3** was also studied by uv spectroscopy in Tris buffer solutions of pH 7.4–7.6. Continuous variation (Job) plots[7] indicate the formation of 1:1 complexes. Examination of these plots (inset, Figure 1) shows the curve for 6-thioG to break more sharply than that for 8-thioG. This result suggests the binding constant for 6-thioG to be substantially greater than that for 8-thioG. Equilibrium constants, evaluated spectrophotometrically (Figure 1) by the method described in ref 8, confirm the qualitative results of the Job's plots. For 8-thioG, using data at 310 nm (C=S chromophore), K_1 was found to be $4.8 \pm 1.0 \times 10^5$ l./mol, whereas the analysis of similar data taken at 340 nm for the 1:1 PHMB–6-thioG complex gives a K_1 value of $7.2 \pm 2.6 \times 10^6$ l./mol.[9]

The higher equilibrium constant for the 6-thioG complex may be due to a chelate effect. PHMB bound to sulfur in 6-thioG (**2**) can form a stable five-membered ring by coordinating to N(7) simultaneously. For 8-thioG (**3**), a four-membered ring would result from chelation to N(7). In order to investigate the possibility of chelation directly, the crystal structure of a 6-mercaptopurinepalladium complex was determined. To simulate a riboside, N(9) was blocked by a benzyl substituent. The complex bis(6-mercapto-9-benzylpurine)palladium(II)–dimethylacetamide was synthesized by allowing 1-propanol vapors to diffuse into the reaction solution prepared from the ligand[10] and $PdCl_2$ in dimethylacetamide. The molecular structure, determined in an X-ray crystallographic study to be reported in detail elsewhere, is shown in Figure 2.

The coordination geometry is a slightly distorted square in which two chelating ligands contribute both sulfur and N(7) donor atoms. Distortions of the ligand from the geometry found in 6-mercaptopurine monohydrate[11] result from the *ca.* 0.3-Å decrease in the S---N(7) "bite" distance upon chelation. This structure may be contrasted with the results for a copper complex of 9-methylhypoxanthine (6-oxo-9-methylpurine) in which the metal is bound only to N(7).[12]

Having established that thionucleosides are good ligands for binding class b metal ions,[13] it was of interest to study the interaction of mercury(II) with naturally occurring thiolated bases. Solutions of valine tRNA from *Escherichia coli*[14] were dialyzed to

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