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Communications

Thermochemistry of Fluoroxy Compounds: A Linear Correlation between O–F Bond Energies and ^{19}F Chemical Shifts

Sir:

The class of fluoroxy compounds ROF has been extensively investigated due to the peculiar chemical properties associated with the relatively weak O–F bond.[1–4] They have also found generalized use as propellants[5] and in the synthesis of organic and inorganic fluorinated species.[6] In this communication it is shown that these compounds offer the rather unique example of a linear correlation between bond energies and NMR chemical shifts over wide ranges (13 kcal/mol and 100 ppm, respectively), which include the least and the most stable members of the family.

The prime interest of the reported relationship stems from the possibility of estimating valuable thermochemical data for the O–F bond from the readily accessible ^{19}F magnetic resonance data.[1,7] We submit the view that it also provides further insights into the nature of chemical bonding in fluoroxy compounds and related species and may lead to a better understanding of the general factors determining fluorine resonance shifts.

The major changes observed (Table I) reveal that nuclear magnetic resonance of fluorine is a far more sensitive probe of bonding than alternative techniques, such as infrared spectroscopy. The irregular grouping of OF stretching vibrational frequencies[1] around 910 ± 40 cm^{-1} is to be contrasted with the well-documented correlations between stretching frequencies and energies of bonds involving hydrogen atoms.[8]

Table I. ^{19}F NMR Chemical Shifts and Bond Energies for the OF Group[a]

compd	$-\phi$, ppm	D, kcal/mol	compd	$-\phi$, ppm	D, kcal/mol
CF_3OF	147.1	47.6	$FC(O)OF$	209.0	(40.1)
CF_3CF_2OF	139.4	(48.8)	FSO_2OF	249.0	34.7
$(CF_3)_2CFOF$	153.9	(47.0)	SF_5OF	189.0	43.2
$(CF_3)_3COF$	149.6	(47.6)	ClO_3OF	219.4	(38.8)
$CF_2(OF)_2$	159.2	46.1	NO_2OF	(251.6)	34.7

[a] Values between parentheses are estimated from eq 1.

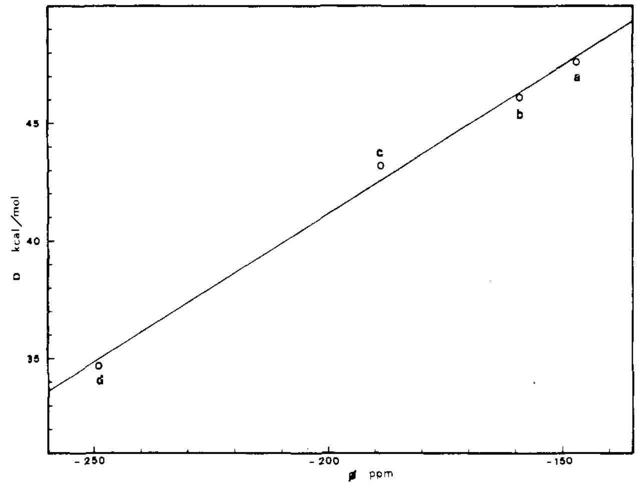

Figure 1. Bond energies D_{RO-F} vs. OF NMR chemical shifts, relative to Cl_3CF, for (a) CF_3OF, (b) $CF_2(OF)_2$, (c) SF_5OF, and (d) FSO_2OF.

At present, a tractable semiquantitative treatment of magnetic shielding for the heavier nuclei based on Ramsey's theory indicates that chemical shifts are dominated by a paramagnetic term arising from local electron density:[9–11]

$$\sigma \approx \sigma_p \approx -\tfrac{2}{3}(e\hbar/mc)^2\langle r^{-3}\rangle \Delta E^{-1}(1 - f_i)$$

where ΔE is the HOMO–LUMO energy gap and f_i a factor proportional to the ionic character of the bond ($f_i = 1$ for F$^-$).[10] Specifically, in the case of ROF compounds it is expected that the ΔE corresponding to the lowest lying (n → π*) electronic transition of the OF group, as well as f_i, should be nearly independent of R. Therefore, variations of σ would then reflect changes in the matrix elements $\langle r^{-3}\rangle$. Since it can be shown that the main contributions to $\langle r^{-3}\rangle$ arise from one-center integrals centered on the F atom,[12] the long-range effects of the R group can be rationalized in this case by assuming that bonding in ROF is due to a delocalized molecular orbital. This is visualized as a three-center–two-electron MO resulting from

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the overlap of a singly occupied R orbital with the π^* SOMO of OF.[13] According to this view, releasing R groups will simultaneously increase the paramagnetic shielding around the fluorine atom *and* the antibonding character of the bond; that is, they will decrease ^{19}F NMR chemical shifts and O–F bond dissociation energies (Figure 1).

This analysis resembles an earlier proposal accounting for trends in bond lengths and force constants in nitrosyls and peroxides.[14] These compounds derive from NO and O_2, which also possess π^* SOMO's. As a contradistinction, the present correlation, probing simultaneously into bond stability and electron distribution, actually discloses the concomitant variations in the population of the relevant π^* MO rather than invoking them.

The ^{19}F nuclear magnetic resonance absorption data for the OF group presented in Table I typically show a large downfield shift relative to trichlorofluoromethane and are out of the range of most other fluorine NMR absorptions.[7] This feature allows the unambiguous assignment of OF absorptions.

The available thermochemistry on the OF bond in CF_3OF, SF_5OF, FSO_2OF, and NO_2OF has been recently reexamined,[4] and the corresponding D_{RO-F} values, calculated from experimental activation energies E and OF stretching vibrational frequencies ν_s as $D = E + 0.5h\nu_s$, are considered reliable to within 1 kcal/mol. Similarly, a lower bound for D_{RO-F} in difluoroxydifluoromethane, $CF_2(OF)_2$, can be derived from a study of its thermal decomposition[15] by assuming a normal A factor ($A = 10^{15.3}$ s^{-1}) for the unimolecular fission of each O–F bond.[4] A linear function between D_{RO-F} (kcal/mol) and ϕ (ppm) relative to Cl_3CF (eq 1) describes well the proposed

$$D = 48.8 + 0.126(\phi + 140) \qquad (1)$$

correlation in the ranges 34.7–47.6 kcal/mol and −147.1 to −249.0 ppm (Figure 1). Equally important, when eq 1 is combined with extensive data on ^{19}F NMR of fluoroxy compounds,[7] the rates of thermal decomposition predicted from the expression $\log k$ (s^{-1}) = $15.3 - E/\theta$ ($\theta = 10^{-3}(4.575T)$ mol kcal^{-1}) are clearly consistent with a large body of qualitative observations. Thus, for example, the greater thermal stability of fluoroxyfluoroalkanes relative to perfluoroacyl hypofluorites[1] certainly reflects their upfield OF fluorine shifts (Table I). In Table I we present estimated values of D for some representative fluoroxy compounds.

On this basis, from the measured value of the ^{19}F shift in ClO_3OF, $\phi = -219.4$ ppm,[16] and using eq 1, we estimate an activation energy for the O–F homolysis of about 37.5 kcal/mol and would predict a fairly stable species below 400 K if this process were rate determining. Since measured rates are more than a factor of 10^3 larger than estimated values, one is led to conclude that perchloryl hypofluorite pyrolysis occurs via a complex mechanism rather than a simple unimolecular reaction in full agreement with experimental observations.[17] It is apparent that eq 1 provides a valuable guide toward the kinetics and thermochemistry of fluoroxy compounds. An extension of these ideas is under way.

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Department of Chemistry **E. Ghibaudi**
University of Mar Del Plata **A. J. Colussi***
7600 Mar Del Plata, Argentina

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Articles

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of the Oxidation of Europium(II) Ions and of the Reduction of Europium(III) Ions by 2-Hydroxy-2-propyl Radicals

S. MURALIDHARAN and JAMES H. ESPENSON*

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The kinetics of the reactions of Eu^{3+} and Eu^{2+} with 2-hydroxy-2-propyl radicals in H_2O and D_2O have been studied by competition methods based on homolysis of (2-hydroxy-2-propyl)pentaaquochromium(III) ions. The radicals react with Eu^{3+} to form Eu^{2+} and acetone with rate constants (±15%) of 3.7×10^4 M^{-1} s^{-1} in H_2O and 8.8×10^3 M^{-1} s^{-1} in D_2O and with Eu^{2+} to form Eu^{3+} and 2-propanol with rate constants of 1.5×10^5 M^{-1} s^{-1} in H_2O and 3.1×10^4 M^{-1} s^{-1} in D_2O at 25 °C. The reduction of Cr^{3+} by $\cdot C(CH_3)_2OH$ is characterized by the rate constant $(5.6 \pm 1.4) \times 10^2$ M^{-1} s^{-1}. Mechanisms consistent with the kinetic data have been formulated.

Introduction

The oxidation–reduction reactions occurring between Eu^{3+} or Eu^{2+} ions and carbon-centered free radicals have received very little attention. The only information we have found concerns a semiquantitative pulse radiolytic study[1] that reports the reduction of Eu^{3+} to Eu^{2+} by the carboxylate radical anion $\cdot CO_2^-$ ($Eu^{3+} + \cdot CO_2^- \rightarrow Eu^{2+} + CO_2$) as having $k > 7 \times 10^6$ M^{-1} s^{-1}. The availability of the 2-hydroxy-2-propyl radical from the homolytic decomposition of an organochromium(III) complex has provided a useful method for studying less reactive substrates, and thus a method of evaluating rate constants for the reaction of a series of cobalt(III) complexes[2a] and pyridinium ions[2b] and for the oxidation of vanadium(II) ions.[3] We

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