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Registry No. *trans*-[Ru(NH_3)$_4$$Cl_2$]Cl, 63251-19-4; *trans*-[Ru(NH_3)$_4$$I_2$]I, 97134-68-4; *trans*-[Ru(NH_3)$_4$(NCS)$_2$]NCS, 97134-70-8; *trans*-[Ru(NH_3)$_4$$O_2$]$Cl_2$, 38882-90-5.

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Extended Correlation between O–F Bond Energies and ^{19}F NMR Chemical Shifts in Fluoroxy Compounds

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Bond energies D_{RO-F} and ^{19}F NMR chemical shifts ϕ markedly depend on the nature of the R group in fluoroxy compounds. It has been shown[1] recently that the direct correlation between D_{RO-F} and ϕ, which is nearly linear over a wide (13 kcal/mol; 100 ppm) range, (1) may be taken as evidence of three-center bonding[2] in these species, (2) is consistent with changes in the electron population of the π^*-SOMO of OF, and (3) reveals the shortcomings of semiquantitative theories of paramagnetic shielding for the fluorine nucleus.[3]

We wish to report now that an extended set of data, including an experimental measurement of ϕ in NO_2OF (ϕ = 220)[4] together with existing values for F_2O_2 (D_{O-F} = 18 kcal/mol; ϕ = 825)[5] and FOH (54 kcal/mol; 21 ppm),[5a,6] confirms the above conclusions but requires an improved correlation to account for the extremely large spans of both parameters. A nonlinear least-squares fit[7] of the S-shaped D vs. ϕ plot (Figure 1) leads to the expression

$$D = 37.1 + 18.1 \tanh [(222.7 - \phi)/117.5] \qquad (1)$$

This correlation provides a useful predictor of the O–F bond energies of fluoroxy compounds from readily accessible spectroscopic data.[8] It also represents a critical test of ab initio calculations of magnetic shielding constants for heavy nuclei.[10]

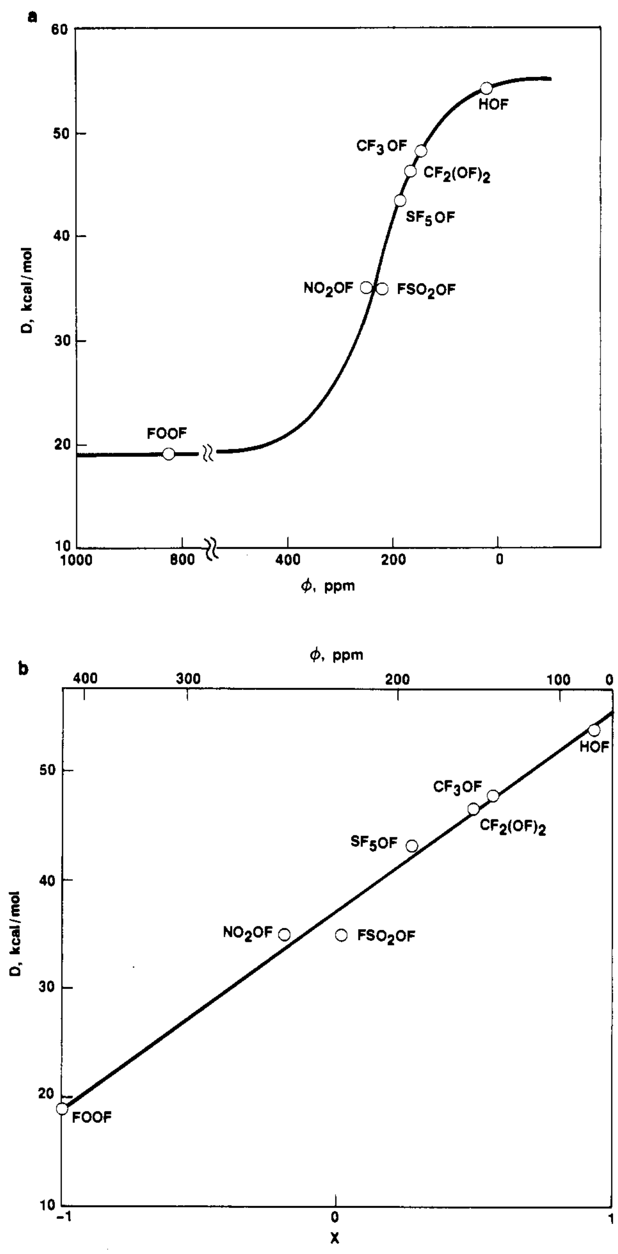

Figure 1. (a) Spectroscopic dissociation energies D_{O-F} vs. ^{19}F NMR chemical shifts ϕ for fluoroxy compounds. (b) D_{O-F} vs. X, where X is tanh [(222.7 − ϕ)/117.5]. The parameters have been determined by using the Marquardt algorithm.[7]

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(4) Determined for neat liquid NO_2OF at 84.6 MHz using $CFCl_3$ as external standard. The measured shift increased from 218.7 ppm at −95 °C to 219.6 ppm at −45 °C. Positive shifts are downfield from $CFCl_3$.

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(8) Thus for example, from experimental observations[9] and an assumption that the marginally stable SF_5OOF decomposes by $SF_5OOF = SF_5OO\cdot + F$ (k_1), followed by the fast reactions $SF_5OO\cdot = SF_5\cdot + O_2$ and $SF_5\cdot + F = SF_6$, we predict from the expression[1] $\log [k_1 \text{ (s}^{-1})] \sim 15.3 - E/(10^{-3}\ 4.575\ T)$ a value for D of about 22 kcal/mol, in good agreement with the one derived from eq. 1 for ϕ = 330. Obviously, overall rates of gas-phase chain reactions or heterogeneous decompositions are partially controlled by D values. The relatively large errors (±1 kcal/mol and probably larger in the case of F_2O_2) usually associated with D values would normally preclude using any such correlation to estimate NMR chemical shifts with a precision comparable to those attained by direct measurement. Notice, however, that ϕ in F_2O_2 changes by about 40 ppm from neat liquid to infinite dilution.[5b]

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