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## PERFLUORINATED ALKOXIDES: SYNTHESIS, STABILITY AND DYNAMIC PROPERTIES

Bruce E. Smart\*, William B. Farnham, William J. Middleton and David A. Dixon

Central Research and Development Department, E. I. du Pont de Nemours &amp; Co., Inc., Experimental Station, Wilmington, Delaware 19898 (U.S.A.)

The availability of isolable tris(dimethylamino)sulfonium (TAS) salts of perfluorinated alkoxides has made it possible to study the relative stabilities and dynamic properties of these fluorinated anions in solution. The rates of fluoride ion exchange in monoalkoxides such as  $\text{CF}_3\text{CFXCF}_2\text{O}^-$  and  $(\text{CF}_3)_2\text{CFO}^-$  were measured by  $^{19}\text{F}$  NMR spectroscopy and were found to be concentration independent, only moderately dependent on structure and solvent, but were markedly slowed by the addition of  $\text{TAS}^+ \text{Me}_3\text{SiF}_2^-$ . By contrast, the exchange rates in fluoroacylalkoxides,  $\text{F}(\text{O})\text{C}(\text{CF}_2)_n\text{CF}_2\text{O}^-$ , were too fast to be determined by  $^{19}\text{F}$  NMR, even at  $-80^\circ\text{C}$ . Experimental data for equilibrium reactions 1 and 2 in both the gas phase and solution are compared to theoretical predictions based on *ab initio* calculations of relative fluoride affinities. The  $\text{CF}_3\text{CF}_2\text{CF}_2\text{O}^-$  anion was found to be ca. 1.5 kcal/mol more stable than  $(\text{CF}_3)_2\text{CFO}^-$ , and it is proposed that the unusual regioselectivity of fluoride ion and other nucleophile attack on hexafluoropropylene oxide is a result of thermodynamic control in late transition states.

