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Theoretical and Experimental Determination of the Proton Affinity of $(CF_3CH_2)_2O$

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ABSTRACT

We report the experimental determination of the proton affinity of the molecule $(CF_3CH_2)_2O$ using chemical ionization mass spectrometry, and we compare it to the theoretical value obtained for protonation at the oxygen atom using the calculational methodology (MP2/6-31G**//MP2/3-21G). The proton affinity for this molecule as measured by bracketing experiments is between 724 kJ/mole and 741 kJ/mole. Ab initio (MP2/6-31G**//MP2/3-21G) calculations yield a value of about 729 kJ/mole, in agreement with the chemical ionization experiments. The results of these and related calculations suggest that the (MP2/6-31G**// MP2/3-21G) methodology is acceptable for estimating the proton affinities of partially- and fully-fluorinated methyl and ethyl ethers. We submit that any conclusions about the chemistry of fluoroether polymer lubricants based on their basicity can also be predicted reliably with such calculations.

INTRODUCTION

The polymeric perfluoroalkyl ethers have been the subject of intense interest in the technical community recently, because of their widespread use as liquid lubricants and their chemical behavior under long-term tribological use (Refs. 1 and 2). Of continuing interest is the chemical degradation which can occur when these fluids interact with metal or metal oxides surfaces in bearings or sliding contacts. There is a great deal of evidence that this degradation involves acid-base chemistry between weakly acidic surface sites and basic sites on the lubricant chain (Refs. 3 and 4).

The proton affinity (PA) of simple fluoroether molecules has been used to characterize their reactivity to surface acid sites. The primary experimental methods used for measurement of gaseous proton affinity use ion cyclotron resonance (ICR) spectroscopy for measurement of the proton transfer to another base, or chemical ionization (CI) measurements to "bracket" the compound between two bases of known PA. These measurements are experimentally difficult to perform and interpret (Ref. 5). Their accuracy depends upon the presence of chemical equilibrium between the species, a certainty in the local temperature in the measurement cell, and the assumption that the rotational and vibrational components of ΔS_T are zero or known. In addition, there may be uncertainty as to the site of protonation on the molecule. Despite these difficulties, there exists a scale of relative proton affinities which is well-established and well-accepted (Ref. 6).

An alternative to the measurement of proton affinities of small molecules is their determination through the use of high-level computational chemistry. Modern computational chemical methods can yield very accurate values for the proton affinity of molecules composed of first-row elements (Ref. 7). Delhalle et al. (Refs. 8 and 9) performed Hartree-Fock calculations for a number of small perfluoroether molecules protonated at the oxygen atoms and at fluorine; they reported that, relative to protonation at oxygen, protonation at an α–fluorine gave a substantially higher predicted PA. Orgel, Ball, and Zehe (Ref. 10) included electron correlation and performed calculations for a number of symmetrical partially and fully-fluorinated dimethyl ethers. Their results showed very good agreement with experimental values of the PA's of dimethyl and diethyl ether, but the lack of experimental data for fluoroether PA's prevented comparison.

In this communication, we report the experimental determination of the proton affinity of the molecule $(CF_3CH_2)_2O$ using CI mass spectrometry, and we compare it to the theoretical value obtained for protonation at the oxygen atom using the calculational methodology (MP2/6-31G**//MP2/3-21G). This methodology has been used by the current authors (Refs. 10 and 11) to predict the PA of $(CH_3)_2O$ and $(C_2H_5)_2O$ within the acceptance limits of the more computationally expensive G2 theory, and this work represents in part a test of its applicability to fluorinated molecules.

EXPERIMENTAL

Chemical ionization mass spectrometry of $(CF_3CH_2)_2O$ was performed on a Finnigan TSQ-45 gas chromatograph/mass spectrometer using its standard CI sample volume with a filament as its electron source. The temperature of the sample volume was 100 °C. After the reagent gas (H_2O, CH_2O, or CH_3OH) was introduced and a stable discharge was established, the $(CF_3CH_2)_2O$ was introduced and the mass spectrum was measured and evaluated for the presence of $(CF_3CH_2)_2OH^+$. The observation of this ion indicates that the PA of $(CF_3CH_2)_2O$ is higher than that of the reagent gas.

CALCULATIONS

Ab initio calculations were performed using the GAUSSIAN 92 program (Ref. 12) on an IBM RS 6000 workstation or a Cray C-90 supercomputer. Geometry optimizations were first performed using the 3-21G basis set with an MP2 correction, and the resulting geometry was used for MP2 single point energy calculations with the 6-31G(d,p) basis set (designated MP2/6-31G**//MP2/3-21G). Initial geometries were chosen as the all-trans configurations (Refs. 13 and 14). The ether was assumed to protonate at the oxygen atom. Thermal energies were simultaneously computed, and the ΔH_{298} for the protonation reaction was determined using:

$$\Delta H_{298} = \Delta E_0 + \Delta E_{\text{therm}} + \Delta(PV) \tag{1}$$

where ΔE_0 is the difference in the total electronic energies of the species at 0 K, and ΔE_{therm} includes contributions from zero-point vibrational energy differences, thermal vibrational energy differences, rotational energy differences, and thermal translational energy differences. $\Delta(PV)$ is the standard conversion from internal energy to enthalpy and for all proton affinity reactions equals –RT (= –2.48 kJ/mol). All vibrational frequencies were scaled by a factor of 0.95 for thermochemical calculations.

RESULTS AND DISCUSSION

The molecular ion for $(CF_3CH_2)_2O$ appears at 182 amu, with the protonated form at 183 amu. The strongest peak in the proton CI spectra appears at 113 amu and is due to loss of CF_3H from the protonated ether. Also present is a strong peak at 163 amu, due to loss of HF from the protonated molecule. The intensity of the M+1 peak at 183 amu is <3 percent of the strongest peak at mass 113. This illustrates one of the challenges of measuring the mass spectra of protonated fluorocarbons: the facility with which stable fluorine species split off from the energized, protonated molecule.

The proton affinities of H_2O, formaldehyde and methanol are, respectively, 723.8, 741.4, and 773.6 kJ/mole (Ref. 6). CI mass spectra using an H_2O/H_3O^+ discharge resulted in a strong peak at mass 183, indicating efficient ionization of the base molecule by H_3O^+. For $(CF_3CH_2)_2O$ in either a formaldehyde or methanol discharge, however, the mass 183 peak was absent. Thus these experiments show that the proton affinity of bis (2,2,2-trifluoroethylether) (g) is between that of H_2O (g) and CH_2O (g) , or between about 724 and 741 kJ/mole.

All calculations converged on stationary points that were true minima as indicated by vibrational frequency calculations that yielded positive frequencies only. Conformational studies to verify that the final geometries were absolute minima were not performed, but it is our judgement that conformational contributions to the proton affinity are slight. Figures 1 and 2 show the structures of the optimized molecule and its protonated form. A summary of the structural parameters is given in Tables I and II; we plan to publish a more detailed structural analysis in a forthcoming paper (Ref. 11).

The neutral molecule has C_{2v} symmetry, with a coplanar arrangement of all five ether backbone atoms and two of the terminal fluorine atoms. Protonation to $(CF_3CH_2)_2OH^+$ changes the C-O-C bond distances and angles only slightly, but now the terminal carbon atoms have rotated out of the C-O-C plane by 42 degrees, and the CF_3 groups have themselves rotated by a few degrees. The result is an ion with C_s symmetry, with an (O)H—F distance of about 2.12A. This distance is well within the limits that define hydrogen bonding, (Ref. 15) and we suggest that intramolecular hydrogen bonding is contributing to the overall stability of the protonated ether. It is difficult to tell the extent to which the intramolecular hydrogen bonding is contributing to the overall stability, but it may be substantial, based upon common H-bond energies of 10 to 35 kJ/mole (Ref. 15).

Table III lists a summary of the calculated single-point energies of the unprotonated and protonated ethers using different levels of theory, with an indication of the predicted proton affinity. The MP2/6-31G**//MP2/3-21G calculations predict a proton affinity of about 729 kJ/mole, in agreement with the chemical ionization experiments. We conclude that calculations at this level can be considered reliable for predicting the proton affinities of related compounds.

Earlier work (Ref. 10 and 11) showed that MP2/6-31G**//MP2/3-21G calculations did a very good job of predicting proton affinities of dimethyl ether and its fluorinated derivatives. In several cases, the calculational results approached the level of performance expected for the G2 level of theory (Ref. 16). We suggest, therefore, that the current methodology is acceptable for estimating the proton affinities of partially- and fully-fluorinated methyl (Ref. 10) and ethyl (Ref. 11) ethers. We further submit that any conclusions about the chemistry of fluoroether polymer lubricants based on their basicity can also be predicted reliably with such calculations. Specifically, the approximately 80 to 100 kJ/mole (excluding intramolecular H-bonding) decrease in the proton affinity which results when diethyl ether is fully fluorinated, indicates that caution must be exercised when attributing perfluoroether lubricant decomposition to acid-base chemistry at oxygen.

REFERENCES

1. P. Herrera-Fierro, W.R. Jones, S.V. Pepper, *J. Vac. Sci. Tech. A* **1993**, 11, 354.
2. J. Pacansky, M. Miller, W. Hutton, V. Liu, A. Scheiner, *J. Am. Chem. Soc.* **1991**,113, 329.
3. M.J. Zehe, O. Faut, *STLE Trans.* **1990**, 33,634.
4. P. Kasai, *Macromolecules* 1992, 25, 6791.
5. M. Meot-Ner, L.W. Sieck, **JACS** 1991,113, 4460.
6. S.G. Lias, J.F. Liebman, R.D. Levin, *J. Phys. Chem. Ref. Data* **1984**, 13, 695.
7. B.J. Smith, L. Radom, **JACS** 1993,115,4885.
8. M. Fontaine, J. Delhalle, M. Defranceschi, G. Lecayon, *Int. J. Quant. Chem.* 1993, 46, 171.
9. M. Fontaine, J. Delhalle, M. Defranceschi, J.M.M. Bourin, *J. Mol. Struct.* 1993, 300, 10.
10. V.B. Orgel, D.W. Ball, M.J. Zehe, *Journal of Molecular Structure(Theochem)* **1997**, 417, 195.

11. M.J. Zehe, D. Ball, “Optimized Structures and Proton Affinities of Fluorinated Diethyl Ethers: An Ab Initio Study,” manuscript in preparation.

12. GAUSSIAN 92. Revisions B and D.2. M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M. W. Gill, M.W. Wong, J. B. Foresman, B.G. Johnson, H. B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzales, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1992.

13. G.D. Smith, R.L. Jaffe, D.Y. Yoon, *Macromolecules* **1994**, 27(12), 3166.

14. G.D. Smith, R.L. Jaffe, D.Y. Yoon, *Macromolecules* **1995**, 28(17), 5804.

15. Pimentel, George C., “The Hydrogen Bond,” Reinhold Pub. Corp., New York, 1960.

16. L.A. Curtiss, K. Raghvachari, G.W. Trucks, J.A. Pople, *J. Chem. Phys.* **94** (1991), 7221.

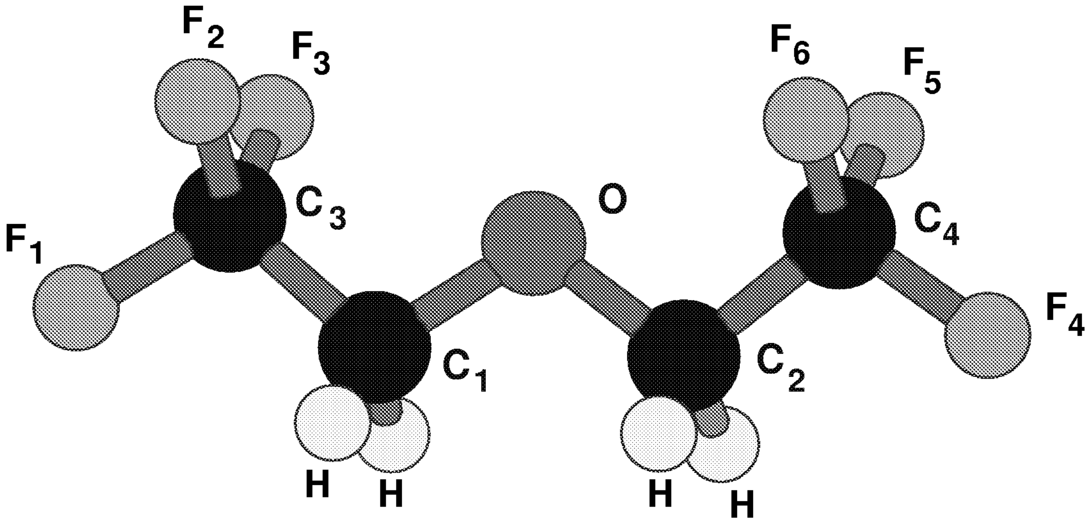

Figure 1.—MP2/3-21G Optimized Geometry for $(CF_3CH_2)_2)$ (C_{2v}).

TABLE I.—MP2/3-21G OPTIMIZED STRUCTURAL PARAMETERS FOR $(CF_3CH_2)_2O$ (C_{2V})

Bond	Value
C1-O-C2	116.0°
C-O	1.46 Å
C1-C3	1.51 Å
C3-C1-O-C2	145.5°
C3-F1	1.38 Å
C3-F2	1.37 Å
F1-C3-C1-O	180°

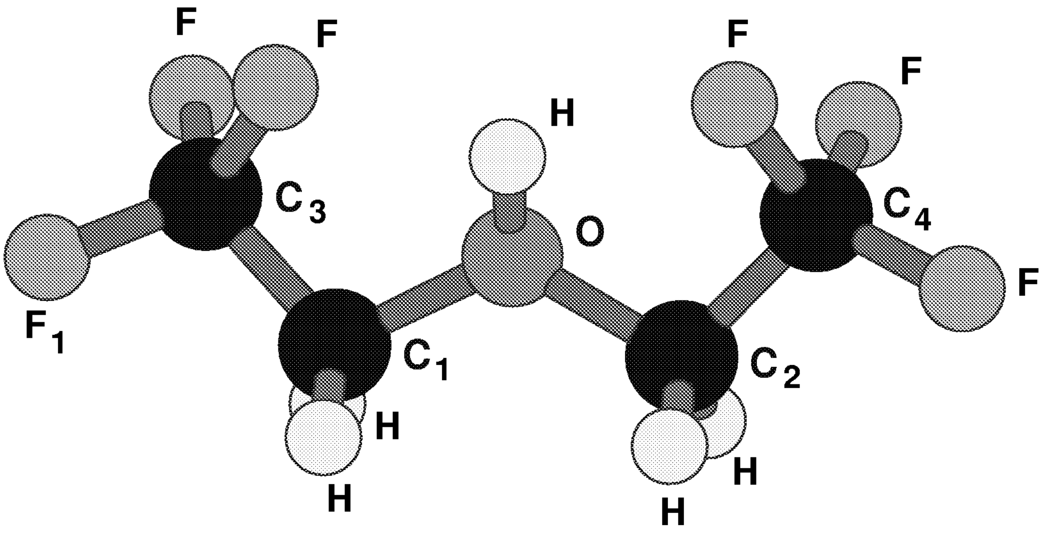

Figure 2.—MP2/3-21G Optimized Geometry for $(CF_3CH_2)_2OH^+$ (C_s).

TABLE II.—MP2/3-21G OPTIMIZED STRUCTURAL PARAMETERS FOR $(CF_3CH_2)_2OH^+$ (C_S)

Bond	Value
C1-O-C2	121.9°
C-O	1.52 Å
C1-C3	1.53 Å
C3-C1-O-C2	169.1°
O-H	1.01 Å
H-O-C1-C3	35.6°
F-H (min)	1.91 Å

TABLE III.—CALCULATED ENERGIES (HARTREES) AND ESTIMATED PROTON AFFINITY FOR $(CF_3CH_2)_2O^+$ BASED ON THE STRUCTURE FROM MP2/3-21G OPTIMIZATIONS

	HF/3-21G	6-31G//MP2/3-21G	6-31G*//MP2/3-21G	6-31G**//MP2/3-21G
$(CF_3CH_2)_2O$	–820.82442	–826.21700	–827.00468	–827.03589
$(CF_3CH_2)_2OH^+$	–821.11574	–826.49085	–827.28370	–827.32412
PA, kJ/mole	736.6	690.7	704.3	728.5

[a] Calculation includes changes in energy due to thermal vibrational and rotational energy and ΔPV; see text for details.

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