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PHOTOELECTRON AND VACUUM ULTRAVIOLET SPECTRA OF A SERIES OF FLUOROETHERS

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SUMMARY

Fluoroethers of the $F(CF(CF_3)CF_2O)_nCHFCF_3$ (n = 1-4) type have their lowest ionization potentials about 3.5 eV higher than ordinary ethers. Their ultraviolet absorption spectra also begin at high frequencies, at about 80000 cm^{-1} or 10 eV. Both spectra are complex indicating the existence of several close lying molecular orbitals in these compounds.

INTRODUCTION

The photoelectron and ultraviolet spectra of saturated ethers have been examined by several authors (1-8). It is well established that the lowest (first) ionization potential in these molecules is due to ejection of an electron from the essentially lone pair orbital concentrated around the oxygen atom and that the electronic transitions giving rise to the bands between 200 and 120 nm also originate in that orbital. Fluoroparaffins have also been studied (7)(9) and it is known that the presence of the fluorine atoms causes large hypsochromic shifts in both the PE and UV spectra. It seemed to us interesting then to perform similar studies on some fluoroethers in order to examine the effect of the fluorines on the oxygen lone pair orbitals and the spectra in general.

The following compounds were studied : $CF_3CF_2CF_2OCHFCF_3$, $F(CF(CF_3)CF_2O)_2CHFCF_3$, $F(CF(CF_3)CF_2O)_3CHFCF_3$ and $F(CF(CF_3)CF_2O)_4CHFCF_3$.

These compounds are increasingly used in industry as heat exchangers and for applications requiring low dielectric constant, high resistivity and high thermal and chemical stability. They are known under the designation freon E-1, E-2, ... etc. For convenience we shall use these symbols in this paper.

EXPERIMENTAL

The samples of fluorinated ethers were supplied by E.I. Du Pont de Nemours and Company of Wilmington, Delaware. Sample purities were checked by infrared absorption, proton magnetic resonance and gas chromatography. The samples were found to have purities of greater than 99.2 wt. % when separated on a 6 m (1.0 cm o.d. stainless steel) column of chromosorb-W with 33 % 'Kel-F' oil No. 3 or on a 3 m (0.5 cm o.d. copper) column of chromosorb-GHP (30/60 mesh acid washed and treated with dimethylchlorosilane) with 5 % 'Krytox'. Impurities are mainly residual homologues of this ether family.

One sample, E-1, was further purified chromatographically in order to verify the vacuum ultraviolet spectrum. After separation of the E-2 and E-3 homologues from E-1, its purity was greater than 99.9 %.

The photoelectron spectra were recorded using a Perkin-Elmer PS-16 spectrometer with a HeI source. Spectra were calibrated using the oxygen 12.08, 12.32, 12,54 and 12.73 eV lines, the nitrogen 15.59 eV line, and argon 15.75 and 15.93 eV lines. Sample pressures of 0.07-0.09 Torr (at the sample inlet) were used and spectra were recorded typically with a counting rate of 4×10^3, a time constant of 4 sec and at 1 mm/min. Ionization potentials quoted are for vertical transitions.

The ultraviolet absorption spectra in the range 50000 cm^{-1} to 95000 cm^{-1} were recorded using a McPherson model 225 1m monochromator. Radiation from a hydrogen discharge was dispersed by a 1200 lines/mm grating before passing to a McPherson model 665 double beam sampling attachment. Linear absorbance was measured with a pair of EMI-6256-S photomultiplier tubes and photon counting electronics. Details have been given previously (10,11). The vacuum UV absorption spectrum is shown with molar extinction coefficient plotted against wavenumber and was obtained with a sample pressure of 0.15 Torr in a 9.0 cm cell having LiF windows. A slit width of 20 μ was used from 95000 cm^{-1} to 65000 cm^{-1} and 5 μ below 65000 cm^{-1}.

Some difficulty was encountered in stabilizing the sample inlet pressure for the photoelectron work. The problem increased from E-1 to E-4 in the order of increasing boiling point and viscosity. Attempts to record E-5 photoelectron spectra were unsuccessful since a very low vapour pressure material appeared to form at the inlet port.

RESULTS AND DISCUSSION

The first peak in the PE spectrum of E-1 is at 13.9 eV. The band is broad, however, with the onset at about 12.6 eV (Fig. 1). Since the assignment of this band is the most important point of this study we will discuss it first. In saturated ethers the first IP has a much lower value. For dimethylether, diethylether, diisopropylether and tetrahydrofuran the vertical values are at 9.94, 9.51, 9.35 (7) and 9.46 eV (8) respectively. Thus the oxygen lone pair orbital ($\bar{O}$) is stabilized by about 3.5 eV, a fact that goes a long way towards explaining the chemical stability and very low associability of E-1 and similar compounds. Since the $\bar{O}$ IP is that high the question arises whether or not it is still a mainly $\bar{O}$ orbital that is the highest occupied molecular orbital in the fluoroethers as it is in the ethers. In perfluoroparaffins the highest occupied orbital is known to be mainly populated in the C-C bonds; the first IP for CF_4, C_2F_6, C_3F_8, n-C_4F_{10}, n-C_5F_{12} and n-C_6F_{14} are 16.20, 14.48, 13.70, 13.30, 13.04 and 12.74 eV respectively according to the data of Robin and his

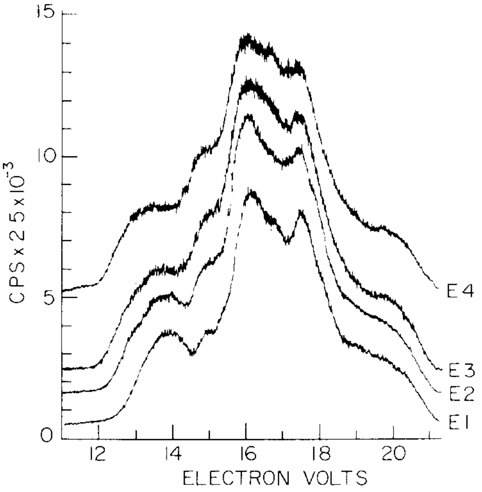

Fig. 1 The photoelectron spectra of $F(CF(CF_3)CF_2O)_nCHFCF_3$ with n = 1,2,3 or 4 (E-1, E-2, E-3, E-4).

coworkers (7). It is thus quite possible that the broad band for E-1 centered at 13.9 eV contains contributions from one or more IP's due to ionization from orbitals of mainly C-C character. In nonfluorinated ethers the second IP is widely separated from the first one, by about 1.6 eV. It is due to an orbital having a large population around the oxygen atom but less than for the highest occupied orbital. This ionization potential is likely to move to much higher frequencies in the fluoro-ethers. A MO with a significant population in the single C-H bond might also contribute to the high energy side of the PE band at 13.9 eV. (The lowest IP is at 14.8 eV for CHF_3 (12)(13); in molecules such as CH_3-CHF_2 or CH_3-CF_3(14) the highest occupied MO is of C-C character. Thus the C-H is not expected to intervene at low energies). The PE bands which follow at higher energies must originate from orbitals of mixed C-O, C-C, C-H, $\overline{F}$ and C-F character with the many fluorine lone pair and bonding C-F orbitals contributing more and more at higher frequencies. In saturated molecules such orbitals usually have IP's above 15.5 eV. Probably none of the apparent peaks corresponds to only one distinct process of ionization.

The PE spectra of E-2, E-3 and E-4 are very similar to that of E-1 (Table I). The maximum of the first band shifts by -0.42 eV in going from E-1 to E-4. This is consistent with changes due to increasing chain length, such as observed for the dimethyl, diethyl and diisopropyl ethers mentioned above.

We shall present the ultraviolet spectrum of only E-1 since the spectra of our other compounds are expected to be similar and to yield no additional information. The onset of UV absorption for E-1 is at very high frequencies (Fig. 2). This is in keeping with the high first IP as well as with the spectra of fluoroparaffins which are among the most translucent compounds that exist. The bands in the

TABLE 1

Vertical ionization potentials of $F(CF(CF_3)CF_2O)_nCHFCF_3$ with $n = 1,2,3$ and 4. (E-1, E-2, E-3, E-4).

n = 1	n = 2	n = 3	n = 4
eV	eV	eV	eV
13.17 sh	12.78 sh	12.96 sh	
13.89	13.77	13.78	13.47
14.90	14.87	14.87	14.96
16.17	16.18	16.20	16.22
16.82 sh	16.99 sh	16.90 sh	16.81 sh
17.51	17.56	17.49	17.53
20.48	20.21	20.33	20.12

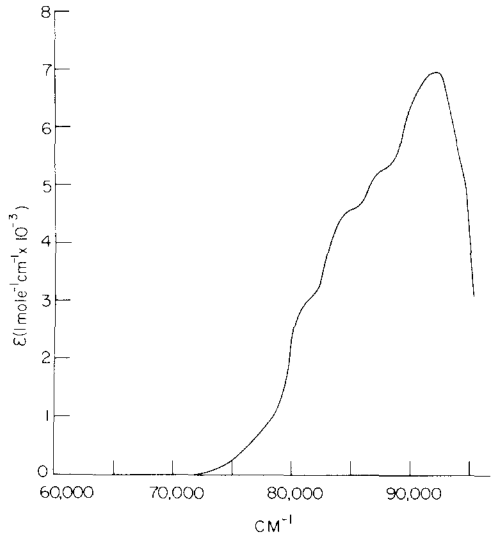

Fig. 2 The vacuum ultraviolet absorption spectrum of $CF_3CF_2CF_2OC$ (E-1). Wavenumbers in cm^{-1} against molar extinction coefficients in liters $mole^{-1}$ cm^{-1}.

spectrum of E-1 are broad. We find shoulders with centers near 81000, 84500 and 87500 cm^{-1} and a band maximum at 92000 cm^{-1}. Just as in the case of the photoelectron bands, none of these seems to be due to a single electronic transition. Both Rydberg and valence-shell transitions might contribute to the observed intensity. The observed broad bands do not enable us to make specific assignments, however.

CONCLUSIONS

The coincidence of several bands in both the PE and UV spectra leads to the frustating situation that we cannot identify individual bands due to given transitions with any degree of certainty. The main conclusion is that fluorinated ethers of the E-1,... type have their lowest IP's at very high values, above 13 eV, and that the highest orbitals of $\bar{O}$ and C-C character must lie close to each other. Correspondingly the ultraviolet spectra also begin at very high frequencies.

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