Electron Affinities of Fluorinated Phenoxy Radicals

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The electron-capture coefficients for five fluorophenoxy phenyl ethers have been determined by using "short" pulse intervals. The temperature dependence of the electron-capture coefficients can be used to determine the electron affinities of the molecules and the fluorophenoxy radicals; the latter providing the bond dissociation energies are known. The molecular electron affinities which have been determined are as follows: pentafluoroanisole, 12.5 ± 2 kcal/mol; 2,3,4,6-tetrafluoroanisole, 5 ± 2 kcal/mol; and 3-fluorophenyl benzyl ether, 6.5 ± 2 kcal/mol. A bond dissociation energy of 75 ± 2 kcal/mol is suggested for the loss of the methyl group in the anisoles, and a value of 68 ± 2 kcal/mol for the benzyl ethers which gives the following radical electron affinities: pentafluorophenoxy, 70.5 ± 2 kcal/mol; 2,3,5,6-tetrafluorophenoxy, 63.5 ± 2 kcal/mol. These results have been illustrated by using two-dimensional Morse potential energy functions. In the case of the pentafluoroanisole, the Morse potentials allow a direct comparison of the current results with electron beam data.

Introduction

The electron attachment to aromatic halides in the presence of oxygen can result in the formation of the aromatic oxy anion.[1] However, in a recent study of the oxygen sensitization of electron-capture response to the perfluoroacetyl derivative of isomers of polycyclic aromatic amines, only the parent negative ion was observed, and for the response to the methoxy derivatives of polycyclic aromatic hydroxides the oxy anion was formed in addition to the parent negative ion in both the presence and absence of oxygen.[2] In order to better understand the energetics of the oxygen anion reaction with aromatic compounds, the electron affinities of some substituted phenoxy and phenyl radicals were determined.

The pulse sampling technique for the study of electron attachment to molecules can be used to determine these radical electron affinities providing compounds are chosen which lead to these anions upon dissociative electron attachment and the bond dissociation energy is known. This has been applied to the CH_3COO and NO_2 radicals.[3,4] In order to use this technique, the negative ion potential energy curve must cross that of the neutral below the dissociative limit so that $E^* = \Delta E$ for the process.[5] This is illustrated in Figure 1 where

$$E^* = \Delta E = D_{AB} - EA_B \tag{1}$$

where EA_B is the electron affinity of B, and D_{AB} is the bond dissociation energy. If the electron-capture-detector (ECD) data have a temperature dependence in the γ region, the E^* can be evaluated from the slope of the conventional ln $KT^{3/2}$ vs. $1/T$ graph.[5] It has been recently shown that ECD data at "short" pulse intervals can be used in a manner similar to data at steady-state conditions to study electron-attachment processes.[6] The advantages of using data at short intervals are a higher standing current and less interference from impurities in the solvent or carrier gas.

Experimental Section

The chromatographic conditions have been described.[6] The solid samples were weighed on a Mettler H54AR balance while the liquid solutions and the dilutions were prepared with high-quality volumetric equipment. Nanograde hexane (Mallinckrodt) was used to prepare the solutions and was checked for electron-capturing impurities. The anisoles (Aldrich) were used without further purification other than chromatography.

The benzyl phenyl ethers were synthesized by the Williamson reaction.[7,8] Reagent-grade sodium hydroxide (MCB), methanol, pentane, potassium carbonate, and ethyl ether (Fisher) were used. The 99% benzyl bromide, pentafluorophenol, 2,3,5,6-tetrafluorophenol, and 3-fluorophenol were obtained from Aldrich. The potassium carbonate was dried at 170 °C; all of the other reagents were used without further purification.

Since the synthetic procedure was the same for the three compounds, it will be described only for the benzyl tetrafluorophenyl ether.

Sodium Tetrafluorophenoxide. To 2.2 g (13.3 mmol) of the 2,3,5,6-tetrafluorophenol dissolved in 5 mL of methanol was added 0.46 g (11.5 mmol) of sodium hydroxide dissolved in 3 mL of 85% aqueous methanol. The flask was flushed with nitrogen and the solvents were removed at 50 °C under vacuum. The resulting white solid was ground and the last trace of solvent and the excess of phenol were removed by heating the powder at 60 °C at 10 mmHg for 24 h. The yield was 2.12 g (98%).

Benzyl Bromide with Sodium Tetrafluorophenoxide. To 2.1 g (11.3 mmol) of sodium tetrafluorophenoxide was added 2.1 g (12.3 mmol) of benzyl bromide, 1.7 g of potassium carbonate, and 15 mL of acetone. After 35 h at 30 °C, the reaction mixture was poured into 80 mL of deionized water and extracted with ethyl ether. The ether layer was washed several times with 10% aqueous sodium hydroxide and dried over anhydrous potassium carbonate. The solvents were removed and the product was recrystallized from pentane to give 2.70 g (93% yield).

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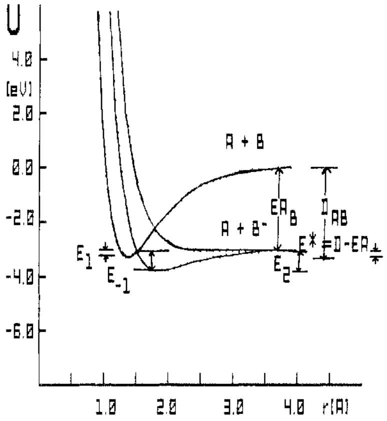
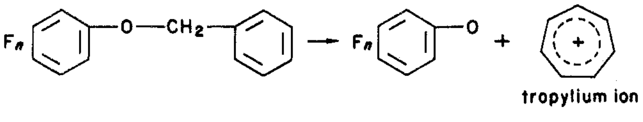


Figure 1. Hypothetical potential energy curves for mechanism IV.

The melting point ranges are 8–12 °C for benzyl tetrafluorophenyl ether, and 44–44.5 °C for the benzyl pentafluorophenyl ether. Only a single major peak was observed on the fid supporting a 95% purity.

Infrared (Beckman Acculab 2), NMR (Varian T-60), and mass (Hewlett-Packard) spectra were obtained. The IR spectra showed a strong band for the stretching mode of the C–O bond in the C–O–C group at 1000 cm^{-1} for the pentafluoro ether and at 1090 cm^{-1} for the others. The aliphatic C–H band is observed at 3070 cm^{-1} while the aromatic C–H stretch is observed at 2940 cm^{-1}. The NMR spectra also show the two types of protons and give the proper ratios. The electron impact mass spectra taken at 20 eV suggest the following fragmentation pattern:



These fragment peaks were present for all three of these compounds, the one at *m/e* 91 (tropylium ion) being the biggest. Only the 3-fluorophenyl benzyl ether showed a peak for the parent molecular ion.

After this study was completed, an atmospheric pressure ionization mass spectrometer (API-MS) was constructed in our laboratory. The conditions within the API source are similar to those within the ECD in our apparatus. In fact, the API source can also be monitored for the free-electron concentration as is done in the ECD. This pulsing did not dramatically affect the ion intensities. The API source contained a conventional nickel-63 foil in close proximity (less than 1 cm) to a pinhole leak into the quadrupole mass spectrometer. Negative ions formed by direct attachment and/or by subsequent reactions in the ECD can be identified by their characteristic *m/e* values provided that their lifetimes are sufficiently long to survive the path from the pinhole through the mass spectrometer (>20 μs). This apparatus was used to identify the ions formed by dissociative attachment in this study. The only ions observed correspond to the phenoxy ions for all of the compounds.

In order to ensure sample purity, the components were separated in a gas chromatograph (Varian 1200) fitted with a bonded-phase capillary column (J & W DB-5 fused silica, 1-μm thickness, 30 m by 0.322 mm). The column temperature was 75 °C and the flow rate 3.5 mL/min. The effluent from the column was simultaneously detected by a flame ionization detector and an electron-capture detector, as well as the API-MS. Thus, the major component can be identified. In our experience, such a procedure is necessary because small amounts of impurities with large electron-attachment rates can frequently dominate the electron-capture response if they are not adequately separated from the compounds of interest. Proper adjustments to the purity of the compounds can also be made by using the response of the flame ionization detector. Note that errors in this quantity will only affect the absolute magnitude of the response and not the energetics obtained from the ECD. However, the errors of the first kind in which a component is not resolved will give invalid responses and eneregetics.

Kinetic Model

The kinetic model for electron capture is summarized in the following reaction sequence:

$$\beta + (\text{Ar} + 10\%\ \text{CH}_4) \xrightarrow{k_p R_\beta} \text{e}^- + \oplus + \text{R} + \beta^* \tag{2}$$

$$\text{e}^- + \oplus \xrightarrow{k_D} \text{neutral species} \tag{3}$$

$$\text{e}^- + \text{AB} \xrightarrow{k_{12}} \text{A} + \text{B}^- \tag{4}$$

$$\text{e}^- + \text{AB} \xrightarrow{k_1} \text{AB}^- \tag{5}$$

$$\text{AB}^- \xrightarrow{k_{-1}} \text{AB} + \text{e}^- \tag{6}$$

$$\text{AB}^- \xrightarrow{k_2} \text{A} + \text{B}^- \tag{7}$$

$$\text{AB}^- + \oplus \xrightarrow{k'_{\text{N1}}} \text{neutral species} \tag{8}$$

$$\text{B}^- + \oplus \xrightarrow{k'_{\text{N2}}} \text{neutral species} \tag{9}$$

where AB represents any polyatomic molecule capable of capturing or attaching an electron, β^* designates the β particle with reduced energy as a result of ion-pair formation, and the other k's are standard kinetic rate constants.

An analysis of this kinetic mechanism using data at short pulse intervals has been carried out,[6] assuming steady state for the negative ion, AB$^-$. The integrated rate expression showing the change in electron concentration is given by eq 10

$$\frac{b - [\text{e}^-]}{b} = \left\{ k_{12} + \frac{k_1(k_2 + k'_{\text{N1}}[\oplus])}{(k_{-1} + k_2 + k'_{\text{N1}}[\oplus])} \right\} \frac{t_p}{2} [\text{AB}] = K[\text{AB}] \tag{10}$$

where [e$^-$] and b are the electron concentrations with and without capturing species, t_p is the time interval between pulses (less than 100 μs), and K is the capture coefficient. Equation 10 differs from the general solution at steady state in the presence of the $t_p/2$ and the absence of $1/k_D$.[5]

For most of the compounds considered in this study, the attached electron occupies a delocalized molecular orbital spread out over the phenyl ring and substituents and the reactions are endothermic so that the direct dissociative mechanism is not likely and k_{12} is assumed to be zero. Equation 10 can take on different forms depending on the relative magnitudes of the rate constants. These are designated α, β, γ, and δ mechanisms and a transition can take place from one region to another as the temperature is changed.

(α) $k_{-1} > k'_{\text{N1}}[\oplus] > k_2$

(β) $k'_{\text{N1}}[\oplus] > k_{-1} > k_2$

(γ) $k_{-1} > k_2 > k'_{\text{N1}}[\oplus]$

(δ) $k_2 > k_{-1} > k'_{\text{N1}}[\oplus]$

For the α mechanism

$$\frac{b - [\text{e}^-]}{b} = \frac{k_1 k'_{\text{N1}}[\oplus] t_p}{2k_{-1}} [\text{AB}] = K[\text{AB}] \tag{11}$$

substituting the statistical mechanical expression for the thermodynamic equilibrium constant $(k_1/k_{-1})^5$ into eq 11 and taking logarithms, we obtain

$$\ln KT^{3/2} = \ln \frac{k'_{\text{N1}}[\oplus] t_p}{2} \frac{A_1}{A_{-1}} + \frac{\text{EA}}{RT} \tag{12}$$

where A_1/A_{-1} can be determined from fundamental constants, EA is the molecular electron affinity, and R is the gas constant. If $k'_{\text{N1}}[\oplus]$ is temperature independent, the EA of the molecule

TABLE I: Temperature Dependence Parameters for Anisoles and Benzyl Phenyl Ethers[a]

compd	$A_1/20$[b]	$400A_2$[c]	E_1[d]	E_2[d]	E_{-1}[d]	EA(AB)[d]	E^*[d]
pentafluoroanisole	2.0×10^{12}	5×10^{11}	0.5	17.0	13.0	12.5	4.5
2,3,5,6-tetrafluoroanisole	1.5×10^{12}	4×10^{12}	3.0	16.8	8.0	5.0	11.8
pentafluorophenyl benzyl ether	2.0×10^{11}	4×10^{11}	−0.5	13.0	16.0	(16)	(−3)
2,3,5,6-tetrafluorophenyl benzyl ether	2.0×10^{13}	8×10^{13}	0.0	12.8	8.0	(8)	4.8
3-fluorophenyl benzyl ether	2.0×10^{12}	1×10^{12}	3.5	14.5	10.0	6.5	8.0

[a] $k_N = 2500\ \mathrm{s}^{-1}$; $A_1/A_{-1} = 10^{12.5}$. [b] Units: 1/(mol s). [c] Units: s^{-1}. [d] Units: kcal/mol.

TABLE II: Parameters Utilized To Calculate Potential Energy Functions[a]

compd		$\mathrm{EA_B}$[b]	D_{AB}[b]	k_{A}	k_{R}	k_{B}
pentafluoroanisole	(a)	70.5	75	0.60	1.53	1.00
	(b)	70.5	75	0.09	1.49	1.00
2,3,5,6-tetrafluoroanisole		63.5	75	0.54	1.25	1.00
pentafluorophenyl benzyl ether		70.5	68	0.46	1.05	1.00
2,3,5,6-tetrafluorophenyl benzyl ether		63.3	68	0.44	0.92	1.00
3-fluorophenyl benzyl ether		60.2	68	0.55	1.41	1.00

[a] $r_e = 1.4$ Å; $\nu_e = 1000\ \mathrm{cm}^{-1}$. [b] Units: kcal/mol.

can be determined from a plot of ln $KT^{3/2}$ vs. $1/T$.

At high temperatures, the negative ion AB^- may dissociate, which we refer to as the γ region. In this case $k_2 > k'_{\mathrm{N1}}[\oplus]$ and eq 10 gives

$$K = k_1 k_2 t_p/(2k_{-1}) \tag{13}$$

In the δ and β regions eq 10 gives

$$K = k_1 t_p/2 \tag{14}$$

and there will be very little temperature dependence. In some cases, three regions are observed so that it is necessary to use the complete equation 10.

$$K = \frac{t_p}{2}\left[A_{12}e^{-E_{12}/RT} + \frac{\dfrac{A_1}{T^{1/2}}e^{-E_1/RT}(A_2Te^{-E_2/RT} + A_N)}{(A_{-1}Te^{-E_{-1}/RT} + A_2Te^{-E_2/RT} + A_N)}\right] \tag{15}$$

Potential Energy Functions

It has been shown[15,16] that two-dimensional potential energy functions can be used to describe the different mechanisms of the electron attachment to molecules. The Morse potential referenced to zero potential at infinite separation was selected to approximate the potential energy of the neutral. This is written as

$$U(\mathrm{AB}) = -2D_{\mathrm{AB}}{}^0 \exp(-\beta(r - r_e)) + D_{\mathrm{AB}}{}^0 \exp(-2\beta(r - r_e)) \tag{16}$$

where

$$D_{\mathrm{AB}}{}^0 = D_{\mathrm{AB}} + \tfrac{1}{2}h\nu_0 \tag{17}$$

$$\beta = \nu_0[2\pi^2\mu/D_{\mathrm{AB}}{}^0]^{1/2} \tag{18}$$

ν_0 is the fundamental frequency, μ is the reduced mass, r_e is the equilibrium internuclear distance, and r is the internuclear distance.

A modification of the Morse potential for the neutral molecule was used to approximate the potential energy function of the negative ions of the halogens as follows:[18]

$$U(\mathrm{AB}^-) = -2k_{\mathrm{A}}D_{\mathrm{AB}}{}^0 \exp(-k_{\mathrm{B}}\beta(r - r_e)) + k_{\mathrm{R}}D_{\mathrm{AB}}{}^0 \exp(-2k_{\mathrm{B}}\beta(r - r_e)) + \mathrm{EA_B} \tag{19}$$

The quantities k_{A}, k_{R}, and k_{B} are dimensionless parameters while $\mathrm{EA_B}$ is the electron affinity of the radical or atom which carries the negative charge upon dissociative electron capture. The quantities k_{A} and k_{R} can be determined from the vertical attachment energy and the molecular electron affinity as shown in ref 18. The value of k_{B} can be taken as 1.0 for ions with low bond dissociation energies (less than 10 kcal/mol). The probability distribution for the electron impact cross section can be determined in a limiting case of unit survival factor from the potential energy curves of the negative ions as shown in ref 18 by using

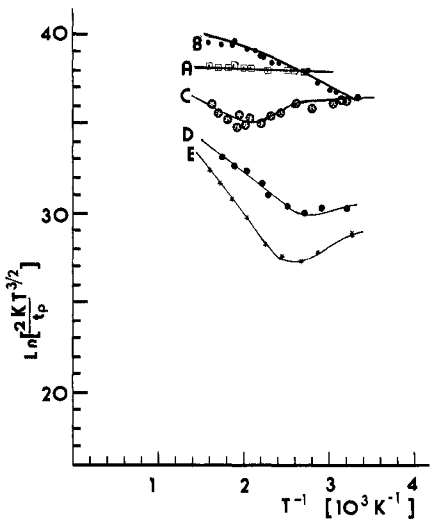


Figure 2. Temperature dependence of electron-capture coefficient. The lines correspond to calculations according to eq 15: (A) pentafluorophenyl benzyl ether, (B) tetrafluorophenyl benzyl ether, (C) pentafluoroanisole, (D) tetrafluoroanisole, (E) 3-fluorophenyl benzyl ether.

$$P(E_v) = \frac{1}{v}\frac{(\alpha/\pi)^{1/2}}{2^n n!}(H_n(\zeta))^2 e^{-\zeta^2} \tag{20}$$

where

$$\alpha = (\mu f/\hbar^2)^{1/2} \tag{21}$$

v = velocity of the electron, μ = reduced mass, f is the force constant for the bond to be broken, n is the vibrational quantum number, $H_n(\zeta)$ are the Hermite polynomials, and

$$\zeta = a^{1/2}(r - r_e) \tag{22}$$

Results and Discussion

The electron-capture data and the calculated curves using eq 15 are listed in Figure 2. The parameters for the curve are shown in Table I. Also given in Table I are the experimental values of E^* and the molecular EA. The values in parentheses are not experimental values. In Figure 3 semiempirical Morse potential energy curves (eq 16, 19, and 20) and the experimental electron impact data from ref 20 are given for pentafluoroanisole while

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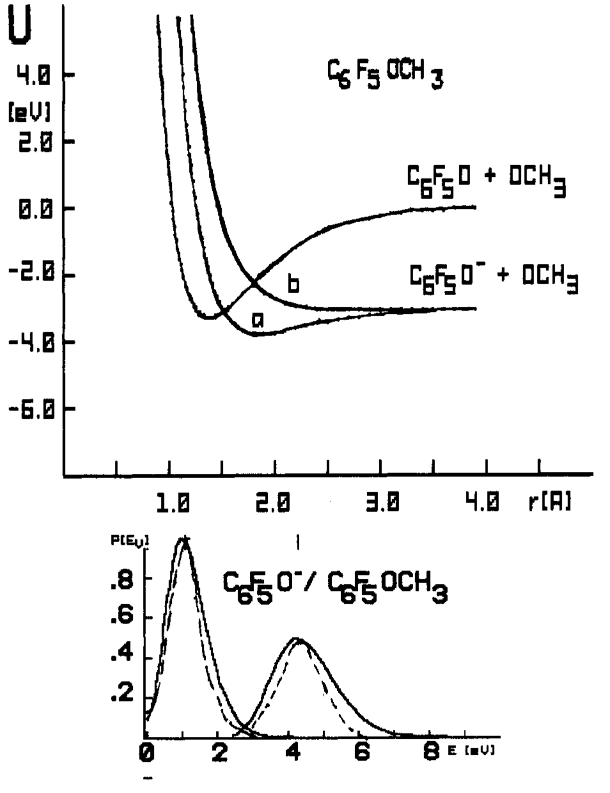

Figure 3. AB, AB⁻, and AB⁻* potential energy curves for pentafluoroanisole. $P(E_v)$ curves: (—) calculated, (- - -) experimental.

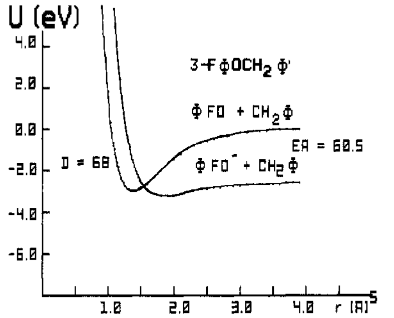

Figure 4. AB, AB⁻, and AB⁻* potential energy curves for 3-fluorophenyl benzyl ether.

the Morse potentials for 3-fluorophenyl benzyl ether are shown in Figure 4. The parameters used to obtain these curves are shown in Table II.

At high temperatures all of the compounds except for the pentafluorophenylbenzyl ether have a negative slope corresponding to a dissociative mechanism (i.e., a γ region). The data for the anisoles and the monofluorophenyl benzyl ether show an α region while the pentafluoroanisole data have a β region. Since the dissociative reaction for the pentafluorophenyl benzyl ether is exothermic, the data either are in the γ region or occur unimolecularly or both. In this case, the only quantities which can be determined from the experimental data are A_1 and E_1.

For the other compounds, the data in the α region establish the molecular electron affinity and the value of $k'_{N1}[\oplus]$. However, because of the limited amount of data in this region and because of the overlap of the data in other regions, we have chosen to keep the intercept constant at 20, which corresponds to a value of 2500 s^{-1} for the pseudo-first-order recombination coefficient. Thus, there is a greater than normal error for the electron affinities of about 2 kcal/mol which results from an uncertainty of about ±2 units in the intercept. There are no electron affinities for direct comparison but these results are in the general range of values which have been determined with the ECD,[4] and especially the value for pentafluorobenzene (17.0 kcal/mol).[19]

The activation energy in the γ region, E^*, is more precisely determined so that the intercepts have been actually determined and can be calculated from $12.5 + \ln A_2$ and range from 39 to 41 except for the tetrafluorophenyl benzyl ether at 45. The errors in the E^* values should be about ±1 kcal/mol. Since the phenoxy negative ion should be the product of dissociative attachment to both the anisoles and the benzyl phenyl ethers, the difference between the energy of activation for a given anisole and its corresponding benzyl phenyl ether should be the difference in bond dissociation energy between these compounds. Thus, for the tetrafluorophenyl compounds, the difference is 7 kcal/mol. Unfortunately, there are no reported bond dissociation energies for any of these compounds, and values for the unsubstituted anisole include 60.0,[11] 61.2,[12] 63.8,[13] and 67.0[14] kcal/mol. Therefore, a different scheme was followed in the determination of the electron affinities of the phenoxy radicals. There are two values of the electron affinity of the phenoxy radical: 54.0 kcal/mol from gas-phase affinities[9] and 54.4 kcal/mol from photodetachment.[10] Also, evidence has been presented that the substitution of a fluorine atom in the meta position increases the electron affinity of the radical by 5.8 kcal/mol.[6] Therefore, an electron affinity of 60.2 kcal/mol was assumed for the 3-fluorophenoxy radical, which leads to a value of 68 kcal/mol for the bond dissociation energy of the benzyl phenyl ethers and 75 kcal/mol for the anisoles. This latter value is higher than any reported previously. Using these values for the bond dissociation energies, we can calculate the electron affinities of the radical from the experimental E^* values and eq 1, as given in Table II. An upper limit to the electron affinity of the pentafluorophenoxy radical can be obtained by simply adding the contributions of a single fluorine atom to the phenoxy radical[6] and is 76.4 kcal/mol. This is an upper limit because it is known that the effect of multiple substitutions is less than that for a single substitution. Thus, the value of 70.5 kcal/mol is in reasonable agreement with this value.

Alternatively, one may assume that the recently reported value for the bond dissociation energy for anisole is the same as the fluoro-substituted anisoles. This gives the electron affinity of the pentafluorophenoxy radical as 60 kcal/mol, the tetrafluorophenoxy radical as 53 kcal/mol, and the monofluorophenoxy radical as 50 kcal/mol. The latter value is of course less than the value for the unsubstituted phenoxy radical so that the earlier procedure is preferred.

The electron beam data for pentafluoroanisole were reported by Naff and Compton.[20] When these data are combined with the electron affinities obtained in this work, the lower semiempirical Morse potential energy curve shown in Figure 3 can be calculated. There are two points of comparison which can be made: the width of the distribution, as can be seen in Figure 3, and the calculated activation energy for electron attachment, which is 2 kcal/mol as compared with a value of 0.5 kcal/mol used to calculate the ECD response. The second negative ion curve is obtained by using a primarily dissociative curve and matching the vertical energy. The distribution is again a point of comparison. The activation energy to this curve is 21 kcal/mol but there is no experimental value for comparison.

There are no electron beam data for the other compounds, but by analogy to the pentafluoroanisole, the curves can be drawn to give the appropriate molecular electron affinities and radical electron affinities. In the case of the penta- and tetrafluorophenyl benzyl ethers where the electron affinities are not defined, it has been assumed that the bond dissociation energies of the negative ions are constant at 14.5 kcal/mol. The dissociation energies of the negative ions of the tetrafluoro- and pentafluoroanisoles are constant at 18 kcal/mol. The quantities obtained from these curves have been used to calculate the ECD responses and are shown in Table I. It must be emphasized that these values have not been determined from the ECD data but are consistent with the results.

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Only the E^* values and the molecular electron affinities are experimentally determined. All of the parameters used to calculate the potential energy curves are given in Table II and the consistency of the values, some of which is artificial, should be noted. It would be very interesting to have electron beam or transmission data for these compounds.

In the review of this article, it was pointed out that Naff and Compton[20] observed both the C_6F_5O (m/e 183) ion and the C_6F_4O (m/e 164) ion at low electron energies in the electron impact experiment. It was suggested that this result should be discussed in the light of this paper. In the API–MS experiments, over a wide range of temperatures, the only ions observed for all of the compounds considered in this paper were the phenoxy ions, in contrast to the results cited above.

One possible reason for the difference in the results in the two experiments is the pressure. In the case of the electron beam work, the pressure is very low while the ECD and API experiments are at 1 atm. The formation of the m/e 164 ion requires the breaking of two bonds and the formation of two bonds. At low pressures the ion may have a chance to undergo this rearrangement before it reaches the ground state, but at atmospheric pressure the number of collisions is so great that the ion is rapidly thermalized. Thus, the approach to the rearrangement reaction would have to be close to the intersection of the curves for the neutral and the negative ion, i.e., at E_1. It is also interesting to examine the energetics of the rearrangement reaction. If it is assumed that the product is a cycloether and the ring closure bond is equivalent to a C_6H_5–O bond, then the energetics would be

$$0 = D(\mathrm{CH_3{-}O}) + D(\mathrm{C{-}F}) + \mathrm{EA}(\mathrm{C_6F_5OCH_3}) - D(\mathrm{C_6H_5{-}O}) - D(\mathrm{CH_3{-}F}) - \mathrm{EA}(\mathrm{C_6F_4O})$$

$$0 = 75 + 125 + 12.5 - 90 - 125 - \mathrm{EA}(\mathrm{C_6F_4O})$$

which gives $\mathrm{EA}(C_6F_4O) > 3$ kcal/mol. This is certainly reasonable considering the electron affinities of tetrafluoroanisole and the tetrafluorophenyl benzyl ether.

Conclusions

The temperature dependence of the electron-capture coefficients can be used to determine the electron affinities of the molecules and the fluorophenoxy radicals; the latter providing the bond dissociation energies are known. The molecular electron affinities which have been determined are as follows: pentafluoroanisole, 12.5 ± 2 kcal/mol; 2,3,4,6-tetrafluoroanisole, 5 ± 2 kcal/mol; and 3-fluorophenyl benzyl ether, 6.5 ± 2 kcal/mol. A bond dissociation energy of 75 ± 2 kcal/mol is suggested for the loss of the methyl group in the anisoles, and a value of 68 ± 2 kcal/mol for the benzyl ethers which gives the following radical electron affinities: pentafluorophenoxy, 70.5 ± 2 kcal/mol; 2,3,5,6-tetrafluorophenoxy, 63.5 ± 2 kcal/mol. These results have been illustrated by using two-dimensional Morse potential energy functions. In the case of the pentafluoroanisole, the Morse potential electron impact cross sections agree with electron beam data.

The errors which are quoted above are relative errors based on the ECD data. The precision of the values depend on the errors in the data for the reference compounds and the assumptions given in the discussion.

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Registry No. Pentafluoroanisole, 389-40-2; 2,3,5,6-tetrafluoroanisole, 2324-98-3; 3-fluorophenyl benzyl ether, 72216-35-4; pentafluorophenyl benzyl ether, 1644-67-3; 2,3,5,6-tetrafluorophenyl benzyl ether, 92545-11-4; pentafluorophenoxy, 28384-58-9; 2,3,5,6-tetrafluorophenoxy, 28318-49-2; 2,3,5,6-tetrafluorophenol, 769-39-1; sodium tetrafluorophenoxide, 14055-43-7; benzyl bromide, 100-39-0.

Surface Raman Scattering of Azo Dyes

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The Raman scattering of several azo dyes coadsorbed with pyridine on silver sols is investigated, and their surface spectra and excitation behavior are reported. It is found that the scattering of pyridine is enhanced by a factor of $>10^5$, while that of the dyes is enhanced to a much smaller degree. This effect is most pronounced for dyes that in solution are in resonance with the incident light, in which case the enhancement is many orders of magnitude smaller than for coadsorbed pyridine. Using a "chemical" detuning experiment, it is shown that the enhancement factors of the dyes gradually increase for molecules which are progressively out of resonance.

Introduction

The dependence of the surface enhancement of Raman scattering (SERS) on the molecular nature of the scatterers is basic information which is required for better understanding of this complex phenomenon. A variety of molecules has been investigated to date.[1,2]

One of the more prominent molecular properties is whether it is on resonance or off resonance with respect to the incident light. This may have profound effects on the enhancement of its scattering when adsorbed on a metal surface.

To date, several investigations of the Raman scattering of dye molecules adsorbed on silver were reported.[3-37] There are substantial differences in their results, some claiming full SERS enhancement on top of the resonance enhancement. Others, report smaller surface enhancement factors, but there is a disagreement

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