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Nucleophilic Aromatic Substitution in the Gas Phase: The Importance of F^- Ion-Molecule Complexes Formed in Gas-Phase Reactions between Nucleophiles and Some Alkyl Pentafluorophenyl Ethers

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Abstract: Gas-phase reactions between some alkyl pentafluorophenyl ethers and a number of different nucleophiles have been studied by use of Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy. For $C_6F_5OCH_3$, reaction appears to proceed via three reaction channels, namely, S_N2 substitution on the methyl group, IPSO substitution on the carbon atom bearing the methoxy substituent, and attack on the fluorine-substituted carbon atoms. The nucleophilic aromatic substitution on the fluorine-substituted carbon atoms is apparently the favored reaction channel. This reaction is shown to lead to formation of an F^- ion-molecule complex whose lifetime is long enough to allow reattack by the displaced F^- ion on the newly formed molecule to occur. These secondary reactions are, in order of decreasing facility, proton transfer, E2 elimination, and S_N2 substitution.

Gas-phase ion-molecule reactions have received considerable attention in the last decade as they may help to correlate intrinsic molecular properties and reactivity of chemical species.[1-4] A few reports have described nucleophilic attack on aromatic rings.[5-10] The corresponding reactions can best be rationalized by postulation of anion σ complexes as intermediates. These complexes—often referred to as Jackson-Meisenheimer complexes—are well-known from solution chemistry where they are invoked as intermediates in nucleophilic aromatic substitution reactions which proceed via the addition-elimination pathway (the S_NAr mechanism).[11] Gas-phase reactions between some alkyl pentafluorophenyl ethers and a number of nucleophiles will be described in the present paper. These reactions have been studied by use of Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy.[12]

Polyfluoro-substituted aromatic compounds are known to be susceptible to nucleophilic attack on ring carbon atoms in the liquid phase.[13] Proton abstraction or formation of fluorinated phenoxide ion was observed in gas-phase reactions between fluorine-substituted benzenes and alkoxide ions.[5] In particular, reaction between RO^- and C_6F_6 gave $C_6F_5O^-$ as the major product ion. A similar ion, that is, $CH_3OC_6F_4O^-$, has been observed previously as a product of reaction between OH^- and $C_6F_5OCH_3$ in the gas phase.[6] The formation of these ions resembles closely the production of fluorinated enolate ions in gas-phase systems composed of RO^-/CF_2CF_2[10] or RO^-/CH_2CF_2.[10,14]

This type of gas-phase reaction can be understood more clearly on the basis of F^- ion-molecule complexes formed by nucleophilic aromatic substitution. The observed products are then a consequence of secondary reactions occurring in the F^- ion-molecule complexes. Evidence that strongly supports this view will be presented.

Experimental Section

Experiments were performed with a homemade Fourier transform ion cyclotron resonance (FT-ICR) spectrometer.[15,16] The total pressure was kept normally around 10^{-4} Pa. The ratio of the partial pressures of $C_6F_5OCH_3$, H_2O, and HA (conjugate acid of the nucleophile of interest) was typically 1:0.5-1:0.5-1. In the case of allyl anions the pressure of propene was 2-3 times higher than the pressure of $C_6F_5OCH_3$. The pressures were measured only approximately on an uncalibrated ionization gauge placed in a side arm of the main pumping line.

In a typical experiment the generation of negative ions was carried out with an electron beam pulse of 25-ms duration and an emission current of 600 nA. The electrons were ejected subsequently by a pulse starting during the electron beam pulse and ending shortly thereafter. Negative ions were trapped in the magnetic field of 1.4 T by applying a small negative voltage (-0.8 V) to the trapping plates of the 1 in.^{3} cell.[17] After a chosen trapping time, which in our instrument can be varied up to 6.5 s, the cyclotron motion of the ions was excited by a very fast swept radio-frequency (rf) pulse. The sweeping rate was normally 1.5 ms, the amplitude 2.5 V_{p-p}, and the frequency limits 240-72 kHz, corresponding to the mass range *m/z* 90-300. After monitoring of the image currents induced by the translationally and coherently excited ions in the receiver plates of the cell,[12b] a quench pulse followed. This removes all the ions present in the cell before a new chemistry cycle is started.

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Table I. Primary Negative Ions from $C_6F_5OCH_3$ (M_r 198)

	relative ion yields[a]				
m/z	0 eV[c]	4 eV[c]	6 eV[c]	8 eV[c]	composition[b]
183	89	49	43	43	$C_6F_5O^-$
167		16	36	31	$C_6F_5^-$
164	9	2	3	12	$C_6F_4O^{-}\cdot$
155		12	3	2	$C_5F_5^-$
149				2	$C_6HF_4^-$
148		8	1	2	$C_6F_4^{-}\cdot$
136	2	1	1	1	$C_5F_4^{-}\cdot$
129				3	$C_6F_3^-$
117		12	7	1	$C_5F_3^-$
19			6	3	F^-

[a] Accuracy ±6% on absolute intensities. [b] Given elemental compositions are within error of exact mass measurements. [c] Electron energies are accurate to ±1 eV.

Most of the nucleophiles were generated by proton transfer to OH^-. In the case of deuterated (and also unlabeled) allyl anions, NH_2^- was used to avoid H/D exchange. Both OH^- and NH_2^- ions were formed by dissociative resonance capture of electrons with kinetic energies of 6 eV (H_2O, OH^- is formed via H^-) and 5 eV (NH_3). The $CH_3{}^{18}O^-$ ions were generated from $CH_3{}^{18}ONO$ by using electrons of 50-eV kinetic energy. $N_2O/N_2{}^{18}O$ were used to form $O^-\cdot/{}^{18}O^-\cdot$ (1.2 eV) and CF_4 to form F^- (6 eV). At all electron energies primary negative ions from $C_6F_5OCH_3$ were observed (see Results).

The OH^- and NH_2^- ions and the primary negative ions from $C_6F_5OCH_3$ were ejected 50–100 ms after the electron beam pulse to observe the reactions between the nucleophile of interest and $C_6F_5OCH_3$. The OH^-/NH_2^- ions were ejected with an rf pulse of amplitude 7.1 V_{p-p} and 20-ms duration. The primary negative ions from $C_6F_5OCH_3$ (in the mass range *m/z* 120–200) were ejected with a second rf pulse (amplitude 5 V_{p-p}, 20-ms duration). The relationship between a precursor ion and its product ions was established in all cases by ejection experiments[18,19] or by slight excitation of the cyclotron motion of the precursor ion. Ejection of a nucleophile was normally achieved with an rf pulse (amplitude 2.5–7.1 V_{p-p}, duration 20 ms) starting just after the ejection of the primary negative ions from $C_6F_5OCH_3$. Ejection of a primary product ion was carried out with an rf pulse (amplitude 0.9–3.5 V_{p-p}) starting after the ejection of the primary negative ions and lasting till the start of the excitation pulse. Slight excitation of the cyclotron motion of a primary product ion was typically done after 400-ms delay and with an rf pulse of low amplitude (0.078 V_{p-p}) and short duration (5–10 ms).

Materials. Most of the chemicals used were commercially available. The labeled propenes, 1,1,1-trideuterioacetone, ^{18}O-labeled acetone, $N_2{}^{18}O$, and $CH_3{}^{18}ONO$, used in the present study have been described in previous papers.[20] The trideuteriomethyl pentafluorophenyl ether (about 99% D_3) and ethyl pentafluorophenyl ether were prepared by a Williamson ether synthesis carried out under mild conditions such as in acetone using $CO_3{}^{2-}$ as base.[21a] The CH_3CDO (about 90% D_1) was prepared by oxidation of 1,1-dideuterioethanol using pyridinium chlorochromate as oxidant.[21b] These compounds were purified by preparative GC before use (CH_3CDO: column OV 225, temperature 20–25 °C; $C_6F_5OCD_3$ and $C_6F_5OCH_2CH_3$: column OV 17, temperature 100 °C).

Results

Primary Negative Ion Formation from Pentafluoroanisole. Low-energy electron impact of $C_6F_5OCH_3$ leads to formation of negative ions.[22,23] Spectra recorded at selected electron energies are given in Table I together with the assigned elemental composition of the ions. The molecular anion of $C_6F_5OCH_3$ has not been observed at any electron energy, which is in agreement with the fact that the lifetime of molecular anions of C_6F_5X compounds are of the order of microseconds.[22]

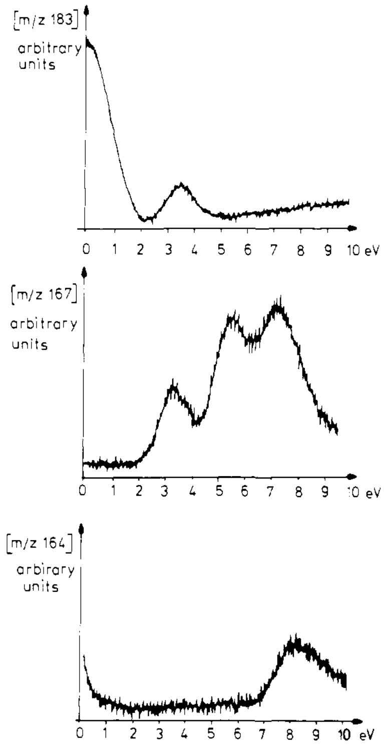

Figure 1. Ionization efficiency curves of the most intense ions in the primary negative ion spectrum of $C_6F_5OCH_3$. Experimental conditions: magnetic field strength, 1.4 T, electron energy, 0–10 eV; filament current, 800 nA; ADC rate, 0.5 MHz; P($C_6F_5OCH_3$), 4.0–8.0 × 10^{-5} Pa.

Ionization efficiency curves of the most intense ions (Figure 1) have been measured with the rapid single ion monitoring computer program developed for the FT-ICR instrument. The electron energy scale was not calibrated, but can be considered accurate to ±1 eV, thus explaining the discrepancy with earlier measurements.[22]

The ions at *m/z* 183 and 167 are formed by dissociative resonance capture.

$$C_6F_5OCH_3 + e \rightarrow \underset{m/z\ 183}{C_6F_5O^-} + CH_3\cdot \qquad (1)$$

$$C_6F_5OCH_3 + e \rightarrow \underset{m/z\ 167}{C_6F_5^-} + CH_3O\cdot \qquad (2)$$

The ion at *m/z* 164 is probably formed via a process involving initial resonance capture giving a radical anion complex composed of F^- and $CH_3OC_6F_4\cdot$. Attack of F^- on the methyl group then leads to the formation of the $C_6F_4O^-\cdot$ radical anion:

$$C_6F_5OCH_3 + e \rightarrow [C_6F_4OCH_3\cdot,F^-]^* \qquad (3a)$$

$$[C_6F_4OCH_3\cdot,F^-]^* \rightarrow \underset{m/z\ 164}{C_6F_4O^-\cdot} + CH_3F \qquad (3b)$$

The ion at *m/z* 155 may be formed by CO loss from the *m/z* 183 ion. The maximum in the ionization efficiency curve of the former ion is found at the same electron energy at which the second maximum in the ionization efficiency curve of the latter ion is observed. Similarly, the *m/z* 136 ion may arise from CO loss from the *m/z* 164 ion. The formation of the ions at *m/z* 148, 129, and 117 can be rationalized by reactions 4–6.

$$\underset{m/z\ 198}{[M^-\cdot]^*} \rightarrow \underset{m/z\ 148}{C_6F_4^-\cdot} + HF + CH_2O \qquad (4)$$

$$\underset{m/z\ 148}{C_6F_4^-\cdot} \rightarrow \underset{m/z\ 129}{C_6F_3^-} + F\cdot \qquad (5)$$

$$\underset{m/z\ 136}{C_5F_4^-\cdot} \rightarrow \underset{m/z\ 117}{C_5F_3^-} + F\cdot \qquad (6)$$

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Table II. Relative Importance of the Reaction Channels in the $C_6F_5OCH_3$ System[a]

nucleophile	S_N2, %	IPSO, %	reacn on F-substituted C atoms, %
oxygen[b]			
HO^-	22	5	73
CH_3O^-	16		84
$CH_3CH_2O^-$	17		83
$(CH_3)_2CHO^-$	14		86
$(CH_3)_3CO^-$	23		77
$(CH_3)_3CCH_2O^-$	15		85
sulfur[c]			
HS^-	78		22
CH_3S^-	31		69
$CH_3CH_2S^-$	29		71
$(CH_3)_3CS^-$	77		23
nitrogen[d]			
NH_2^-	23	6	71
enolate Anions[e]			
$CH_2{=}CHO^-$	34		66
$CH_2{=}C(O^-)CH_3$	20		80
allyl Anions[f]			
$CH_2{=}CH{-}CH_2^-$	9		91
$CH_2{=}C(CN)CH_2^-$	4		96
$CH_2{=}C(CF_3)CH_2^-$	13		87

[a] Normalized to 100%. [b] Trapping time 500–1000 ms. Conversion into products is incomplete for the *tert*-butoxide ion. [c] Trapping time 1000 or 2000 ms. Conversion into products is not complete in any of the cases studied. [d] Trapping time 500 ms. [e] Trapping time 1000 ms for $CH_2{=}CHO^-$, 2000 ms for $CH_2{=}C(O^-)CH_3$. [f] Trapping time 1000 ms. Conversion into products is incomplete for the substituted allyl anions.

Scheme I

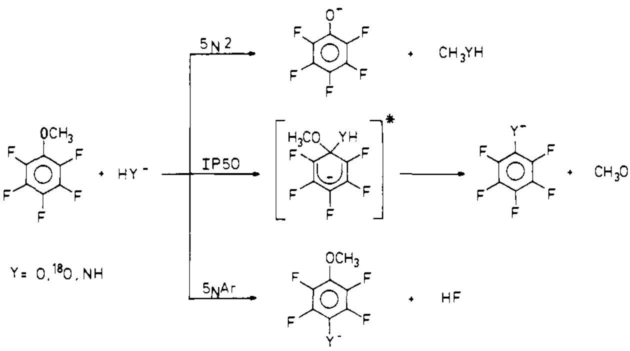

Table III. Product Ions from Reactions of $^{16}O^{-\cdot}$ and $^{18}O^{-\cdot}$ with $C_6F_5OCH_3$[a]

assigned composition[c]	m/z	rel intensity, %[b]		comments
		$^{16}O^{-\cdot}$	$^{18}O^{-\cdot}$[d]	
$C_6F_5{}^{18}OO^-$	201		12	
$C_6F_5O_2^-$	199	11		
$C_7H_3F_4{}^{18}OO^-$	197		10	
$C_7H_3F_4O_2^-$	195	11		
$C_7HF_4{}^{18}OO^-$	195		14	
$C_7HF_4O_2^-$	193	13		
$C_6F_5{}^{18}O^-$	185		30	IPSO
$C_6F_5O^-$	183	100	70	S_N2 + possible charge transfer
$C_6F_4{}^{18}OO^{-\cdot}$	182		24	
$C_6F_4O_2^{-\cdot}$	180	24		
$C_6F_5^-$ or $C_6HF_4{}^{18}O^-$	167	88	100	possible charge transfer
$C_6HF_4O^-$	165	21		
$C_6F_4{}^{18}O^{-\cdot}$	166		58	
$C_6F_4O^{-\cdot}$	164	77	14	possible charge transfer
$C_6F_4^{-\cdot}$	148	7	10	possible charge transfer
unassigned	146	6	3	
$C_5F_4^{-\cdot}$	136	22	21	possible charge transfer
$C_5F_3{}^{18}O^-$	135		5	
$C_5F_3{}^{16}O^-$	133	11	5	
$C_5HF_3^{-\cdot}$	118	22	18	

[a] Trapping time 1000 ms; all primary negative ions from $C_6F_5OCH_3$ have been ejected (see Experimental Section). [b] Accuracy ±6% on absolute intensities. [c] The given elemental compositions are within error of exact mass measurements. [d] The used $N_2{}^{18}O$ contained 72% ^{18}O. The $O^{-\cdot}$ ion has been ejected immediately after the electron beam pulse.

General Reactivity of Pentafluoroanisole. Reaction between $C_6F_5OCH_3$ and the nucleophiles listed in Table II appears to proceed mainly via three different channels. These are S_N2 substitution on the methyl group, IPSO substitution on the carbon atom bearing the methoxy group, and attack upon the fluorine-substituted carbon atoms (designated by S_NAr in Scheme I). The relative importance of these pathways is given in Table II.

S_N2 substitution on the methyl group leads to formation of the $C_6F_5O^-$ ion. This channel is available for all the nucleophiles listed in Table II[24] but dominates only in the cases of SH^- and $(CH_3)_3CS^-$.

IPSO substitution on the carbon atom bearing the methoxy group occurs to some extent with OH^- [6] (see also Table II), with $O^{-\cdot}$ (see Table III), and with NH_2^- (see Table II). Reaction with $CH_3{}^{18}O^-$, however, does not lead to formation of $C_6F_5{}^{18}O^-$, thus indicating IPSO substitution as an unfavorable process for the alkoxide ions.

The favored reaction channel appears to be nucleophilic aromatic substitution on the fluorine-substituted carbon atoms, but the site of attack relative to the methoxy group cannot be determined.[25] It should be mentioned that reaction between methoxide and pentafluoroanisole in methanol as solvent results in formation of dimethoxytetrafluorobenzenes, the percentages of the isomers found being 52% (para), 32% (meta), and 16% (ortho).[26,11a] This might be different in the gas phase and may be strongly dependent on the structure of the nucleophile. However, for reasons of simplicity only para attack will be shown in the reaction schemes.

Oxygen Nucleophiles. The majority of ions formed in reaction between $O^{-\cdot}$ and $C_6F_5OCH_3$ (Table III) involves attack on ring positions,[8] but also product ions that can be ascribed as being due to charge transfer are seen (compare with Table I). The amount of IPSO substitution relative to S_N2 is high in this system (30% IPSO, 70% S_N2). It might be even larger if some of the m/z 183 ions are formed by charge transfer. Although the ^{18}O experiments give some information about the reaction pathways, an unambiguous assignment of mechanism has not been possible for all product ions. A more detailed discussion of this system will not be given therefore in the present context.

Nucleophilic aromatic substitution on the fluorine-substituted carbon atoms by the other oxygen nucleophiles results in two types of product ions, $ROC_6F_4O^-$ and $C_6F_4O_2^{-\cdot}$, as exemplified for the

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(24) The $C_6F_5O^-$ ion is the only observable product ion when F^- reacts with $C_6F_5OCH_3$.

(25) Preliminary experiments on monofluorinated anisoles have indicated that nucleophilic aromatic substitution at the fluorine-substituted carbon atom only occurs in the ortho isomer. The product ion $CH_3OC_6H_4O^-$ generated in the HO^-/*o*-$FC_6H_4OCH_3$ system is, however, not formed via reaction between HO^- and *o*-$FC_6H_4OCH_3$ but indirectly via the $[M-H]^-$ ion of the substrate. Ingemann, S.; Nibbering, N. M. M., work in progress.

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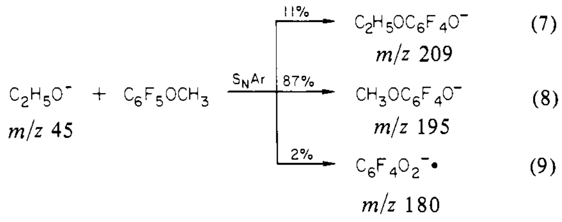
Table IV. Relative Importance of Reaction Channels Available for Reattack by F^- in the Nucleophiles/$C_6F_5OCH_3$ Systems[a]

	mechanism			
nucleophile	proton transfer, %	S_N2, %	E2, %	fragmentation,[b] %
oxygen	$CH_3OC_6F_4O^-$	$ROC_6F_4O^-$ [c]	$CH_3OC_6F_4O^-$	$C_6F_4O_2^{-\cdot}$
HO^-	30			70
CH_3O^-		97		3
$CH_3CH_2O^-$		11	87	2
$(CH_3)_2CHO^-$		6	93	1
$(CH_3)_3CO^-$		4	92	4
$(CH_3)_3CCH_2O^-$		93/4[d]		3
sulfur	$CH_3OC_6F_4S^-$	$RSC_6F_4O^-$	$CH_3OC_6F_4S^-$	$C_6F_4SO^{-\cdot}$
HS^-	100			
CH_3S^-		100[e]		
$CH_3CH_2S^-$		48	52	
$(CH_3)_3CS^-$		29	71	
nitrogen	$CH_3OC_6F_4NH^-$	$H_2NC_6F_4O^-$		$C_6F_4NHO^{-\cdot}$
NH_2^-	3			97

[a] Normalized to 100%. The given elemental compositions of the ions are within error of exact mass measurements. [b] See text. [c] R = alkyl. [d] 93% of ions are $(CH_3)_3CCH_2OC_6F_4O^-$; 4% of ions are $CH_3OC_6F_4O^-$. [e] See text.

$C_2H_5O^-/C_6F_5OCH_3$ system in eq 7–9 (for other systems, see Table IV). The radical anion is the main ionic product in the OH^- case.



Complete ejection of the $CH_3OC_6F_4O^-$ ion formed in this system decreases the abundance of the radical anion only to a minor extent. A slight excitation of the cyclotron motion of the $CH_3OC_6F_4O^-$ ions causes a marked increase of the abundance of the radical anion. The radical anion is formed only to a minor extent with the alkoxide ions (see Table IV). Excitation experiments, however, on the $CH_3OC_6F_4O^-$ ion formed in $C_2H_5O^-$, $(CH_3)_2CHO^-$, and $(CH_3)_3CO^-$ systems and on the $ROC_6F_4O^-$ ion ($(CH_3)_3CCH_2O^-$ system) result in increase of the abundance of the $C_6F_4O_2^{-}\cdot$ radical anion. Excitation experiments on the $ROC_6F_4O^-$ ion in the other alkoxide systems were not reliable, probably due to its low abundance.

Sulfur Nucleophiles. Reaction between the sulfur nucleophiles and $C_6F_5OCH_3$ results in poor conversion into products at the chosen trapping time (see notes to Table II). Figure 2 displays the abundance of reactant ions as a function of reaction time for the cases of $CH_3CH_2S^-$ and $CH_3CH_2O^-$.

Attack on the ring by the sulfur nucleophiles gives rise to similar product ions as in the oxygen systems (Table IV). The $C_6F_4SO^{-}\cdot$ ion, which resembles the $C_6F_4O_2^{-}\cdot$ ion, has not been seen under normal conditions. A minor amount of $C_6F_4SO^{-}\cdot$ (1% of base peak), however, could be observed upon excitation of the $CH_3OC_6F_4S^-/CH_3SC_6F_4O^-$ ions in the SH^-/CH_3S^- systems.

Nitrogen Nucleophiles. Attack on fluorine-substituted ring carbon atoms by NH_2^- gives as the major product a $C_6F_4NHO^{-}\cdot$ radical anion (Table IV). Although reliable excitation experiments on the $CH_3OC_6F_4NH^-$ ion (see Scheme I and Table II) were not possible due to its low abundance, it is most likely the precursor of the radical anion. Another reaction channel giving the $C_6F_5^-$ ion is available in this system. The abundance of this product ion is about 43% of the most abundant ion, $C_6F_4NHO^{-}\cdot$. The formation of $C_6F_5^-$ can be rationalized as proton abstraction and CH_2O loss in a stepwise or concerted manner:

$$\underset{}{C_6F_5OCH_3} + \underset{m/z\ 16}{NH_2^-} \rightarrow \underset{m/z\ 167}{C_6F_5^-} + CH_2O + NH_3 \qquad (10)$$

Enolate Anions. Because the enolate anions are ambident nucleophiles, they are able to react at either oxygen or carbon. Product ions due to attack by both sites are observed (Table V). The product ions arising from initial attack by the oxygen terminus are analogous to the product ions observed in the alkoxide systems (vide supra). The collision complex formed by reaction with the carbon site eliminates either 2HF or HF + CH_3F. In the $CH_2{=}C(O^-)CH_3$ system a radical anion has been observed that corresponds to loss of 2HF + $CH_3\cdot$ from the collision complex.

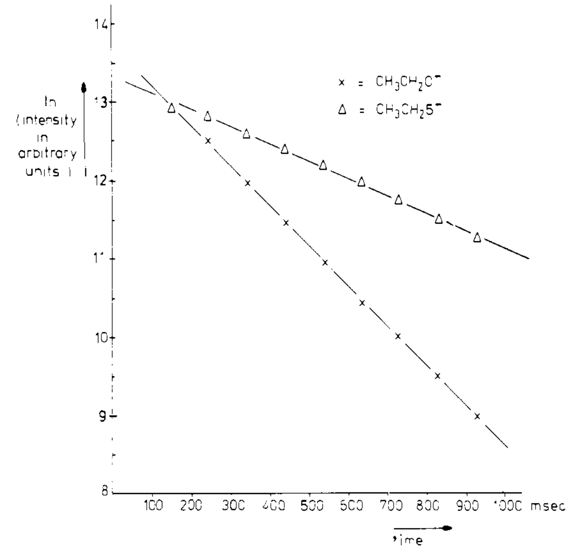


Figure 2. Ln [$CH_3CH_2S^-$] and Ln [$CH_3CH_2O^-$] as function of reaction time with $C_6F_5OCH_3$. Experimental conditions: magnetic field strength, 1.4 T; electron energy, 5.5 eV; filament current, 600 nA; ADC rate, 2 MHz ($CH_3CH_2O^-$) or 1 MHz ($CH_3CH_2S^-$); P($C_6F_5OCH_3$), ~4.0 × 10^{-5} Pa; P(H_2O), ~4.0 × 10^{-5} Pa; P(CH_3CH_2SH) or P(CH_3CH_2OH), ~4.0 × 10^{-5} Pa. An experimental reaction rate constant has not been calculated since the uncertainty in the pressure measurements was judged to be too large.

Table V. Relative Importance of Reaction Channels Available for Reattack by F^- in the Enolate Anions/$C_6F_5OCH_3$ Systems[a]

	mechanism				
	oxygen site attack,[b] %		carbon site attack,[c] %		
nucleophile	S_N2	E2	proton transfer	S_N2	fragmentation,[d] %
$CH_2{=}CHO^-$	25	47	17	11	
$CH_2{=}CDO^-$	24	44	22[e]	9	
$CH_2{=}C(O^-)CH_3$	3	4	83	3	7
$CD_2{=}C(O^-)CH_3$	2	6	81	4	7
$CH_2{=}C(O^-)CD_3$	2	6	83	3	6
$CH_2{=}C(^{18}O^-)CH_3$	2	3	84	4	7

[a] Normalized to 100%. [b] See reactions 24 and 25 and text. [c] See Scheme III and text. [d] See reaction 27 and text. [e] Two-thirds D^+ transfer and one-third H^+ transfer; see reactions 26a and 26b and text.

Scheme II

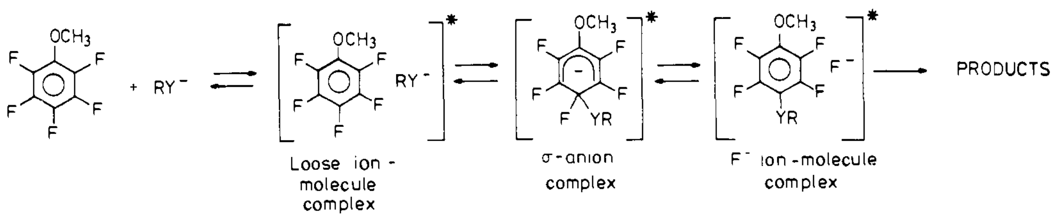


Table VI. Percentages of Product Ions Arising from Attack of Allyl Anions on Fluorine-Substituted Carbon Atoms in $C_6F_5OCH_3$[a]

nucleophile	m/z	rel intensity	composition[b]
$CH_2{=}CHCH_2^-$	204	55	$C_9H_4F_4O^{-}\cdot$
	184	45	$C_9H_3F_3O^{-}\cdot$
$CH_2{=}CDCH_2^-$	205	55	$C_9H_3DF_4O^{-}\cdot$
	185	45	$C_9H_2DF_3O^{-}\cdot$
$CH_2{=}CHCD_2^-$	206	30	$C_9H_2D_2F_4O^{-}\cdot$
	205	28	$C_9H_3DF_4O^{-}\cdot$
	185	42	$C_9H_2DF_3O^{-}\cdot$
$CH_2{=}C(CN)CH_2^-$	224	4	$C_{11}H_5F_3NO^-$
	209	96	$C_{10}H_2F_3NO^{-}\cdot$
$CH_2{=}C(CF)CH_2^-$	267	4	$C_{11}H_5F_6O^-$
	252	96	$C_{10}H_2F_6O^{-}\cdot$

[a] Normalized to 100%. [b] The given elemental compositions of the ions are within error of exact mass measurements.

Slight excitation of the ion corresponding to loss of 2HF from the collision complex increases the abundance of the radical anion.

Allyl Anions. The only observable product ions with the allyl anion as nucleophile are radical anions (Table VI). These ions correspond to loss of either HF + $CH_3\cdot$ or 2HF + $CH_3\cdot$ from the collision complex. Ejection/excitation experiments have proven that the former ion at m/z 204 is not the precursor of the latter ion at m/z 184. The two other substituted allyl anions used as reactant ions give a radical anion as main ionic product as well (Table VI). Also in these cases the observed product ions correspond to loss of either 2HF or 2HF + $CH_3\cdot$ from the collision complex. The low abundance of the former ion has prevented the performance of reliable ejection/excitation experiments.

Discussion

The examples of gas-phase nucleophilic aromatic substitution observed in the present study can be rationalized on the basis of the general reaction scheme (Scheme II). The discussion will be qualitative due to lack of thermochemical data and will mainly be centered around the reaction mechanisms.

Initially there will be a drop in potential energy of the system when the ion approaches the molecule. This is caused by ion-dipole/ion-induced-dipole interactions binding the ion and the molecule together in a loose complex. Energy barriers toward reactions in this loose ion-molecule complex have been observed in some cases[27,28] and have been used to explain the trends in overall reaction rates for a number of reaction types.[28,29] In the present case nucleophilic attack on the fluorine-substituted carbon atoms will lead to formation of a σ anion complex. It is not known whether this is on a local minium or maximum on the potential energy surface describing the reaction. Departure of F^- from the σ anion complex leads to formation of a F^- ion-molecule complex. Simple dissociation of this complex into F^- as ionic product is not observed. Reattack by F^- upon the newly formed molecule takes place instead and leads to new ion-molecule complexes, which subsequently can dissociate into products. In some cases an intramolecular reaction in the primary product ion can give again a F^- ion-molecule complex. Secondary product ions then arise from reattack by this displaced F^-. Although the lifetime of the F^- ion-molecule complexes are unknown, they must live long enough to allow secondary reactions to occur. These secondary reactions can be classified as proton transfer, S_N2 substitution, and E2 elimination.

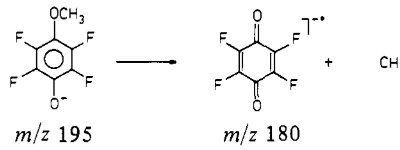
Charge-Localized Nucleophile. Proton transfer to the displaced F^- ion will be the dominant reaction if the neutral in the F^- ion-molecule complex is more acidic than HF. This is the case when the primary reactant ions are OH^-, SH^-, and NH_2^-. In none of these systems has an ion corresponding to reattack on the methyl group been observed (Table IV).

$$C_6F_5OCH_3 + YH^- \rightarrow [CH_3OC_6F_4YH,F^-]^* \rightarrow CH_3OC_6F_4Y^- + HF \quad (11)$$

$$Y = O, S, NH$$

The major part of the even-electron ions $CH_3OC_6F_4Y^-$ undergoes a fast unimolecular reaction to give a methyl radical and a radical anion when Y = O, NH. Collision-induced decomposition, which is achieved by excitation of the cyclotron motion of the long-lived nondecomposing $CH_3OC_6F_4O^-$ ion, leads likewise to formation of the radical anion.

Assuming that the OH^- ion has attacked the para position with respect to the methoxy group, the structure of the radical anion would be as shown in reaction 12.



(12)

In the NH_2^- system an analogous structure for the observed $C_6F_4NHO^{-}\cdot$ radical anion can be written. A radical anion corresponding to $C_6F_4SO^{-}\cdot$ has not been found in the SH^- case, reflecting insufficient energy in the $CH_3OC_6F_4S^-$ ions and/or lower stability of the radical anion. Initial ortho attack of the OH^- and NH_2^- ions would lead eventually to the ortho isomers of the radical anion whereas meta substitution would result in less stable radical anions. The high abundance of the $C_6F_4O_2^{-}\cdot/C_6F_4NHO^{-}\cdot$ radical anions (Table IV) indicates that attack on the meta position by OH^- and NH_2^- is of minor importance if it is occurring at all.

The high electron affinity of p-tetrafluorobenzoquinone (2.92 eV[30]) indicates that its molecular anion is stable. The $CH_3OC_6F_4O^-$ ions must contain sufficient excess internal energy to overcome the barrier toward fragmentation. In the CH_3O^- case the $CH_3OC_6F_4O^-$ ion is formed by a S_N2 reaction of the internal solvated F^- ion. In this system the radical anion is formed only to a minor extent.

$$\underset{m/z\ 31}{C_6F_5OCH_3 + CH_3O^-} \rightarrow [CH_3OC_6F_4OCH_3,F^-]^* \xrightarrow{S_N2} \underset{m/z\ 195}{CH_3OC_6F_4O^-} + CH_3F \quad (13)$$

Reaction 11 for OH^- can be calculated to be approximately 50 kJ/mol more exothermic than reaction 13.[31] This indicates

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[27] Riveros, J. M.; Breda, A. C.; Blair, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 4066–4067.

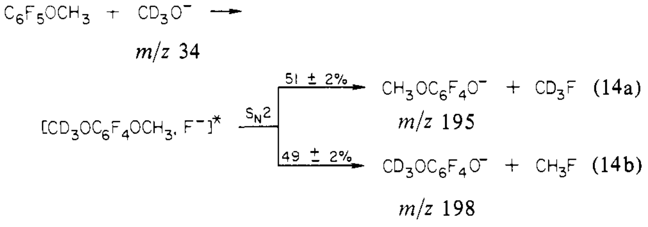
[28] Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219–4228.

[29] (a) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891–7898. (b) Asubiojo, O. I.; Brauman, J. I. *Ibid.* **1979**, *101*, 3715–3724. (c) Pellerite, M. J.; Brauman, J. I. *Ibid.* **1980**, *102*, 5993–5999. (d) Brauman, J. I. *NATO Adv. Study Inst. Ser., Ser. B* **1979**, *40*, 153–164.

[30] Cooper, C. D.; Frey, W. F.; Compton, R. N. *J. Chem. Phys.* **1978**, *69*, 2367–2374.

that the $CH_3OC_6F_4O^-$ ions formed in the proton-transfer process can contain more internal energy than the same ions formed in the S_N2 substitution. It should be emphasized that it is not known how much of the heat of reaction is retained as internal energy within the $CH_3OC_6F_4O^-$ ions. The CH_3F molecules, however, can carry off more of the excess energy than the HF molecules since the number of degrees of freedom is larger.

It is evident from the results that F^- ion–molecule complexes play a decisive role in the formation of products. A direct estimate of the extent to which they are involved is provided by the reaction between CD_3O^- and $C_6F_5OCH_3$:

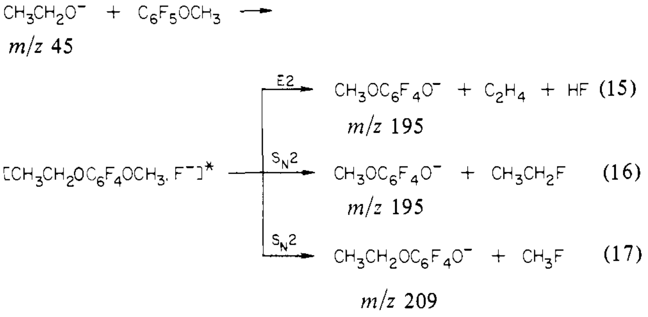


$$C_6F_5OCH_3 + \underset{m/z\ 34}{CD_3O^-} \longrightarrow [CD_3OC_6F_4OCH_3, F^-]^* \xrightarrow{S_N2} \begin{cases} \xrightarrow{51 \pm 2\%} \underset{m/z\ 195}{CH_3OC_6F_4O^-} + CD_3F & (14a) \\ \xrightarrow{49 \pm 2\%} \underset{m/z\ 198}{CD_3OC_6F_4O^-} + CH_3F & (14b) \end{cases}$$

The observed ratio of $[CH_3OC_6F_4O^-]$ to $[CD_3OC_6F_4O^-]$ is within experimental error of unity. The same ratio is obtained in the reaction between CH_3O^- and $C_6F_5OCD_3$, that is, 49 ± 2% $[CH_3OC_6F_4O^-]$ and 51 ± 21% $[CD_3OC_6F_4O^-]$.

The main ionic product is $CH_3OC_6F_4O^-$ when RO^- (R = CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$) reacts with $C_6F_5OCH_3$. Ions corresponding to $ROC_6F_4O^-$ are seen, albeit to a minor extent (Table IV). The decisive role of the F^- ion–molecule complexes is further corroborated by the observation that the same ratio between $[CH_3OC_6F_4O^-]$ and $[CH_3CH_2OC_6F_4O^-]$ is obtained when $CH_3CH_2O^-$ reacts with $C_6F_5OCH_3$ and when CH_3O^- reacts with $C_6F_5OCH_2CH_3$.[32]

With $CH_3CH_2O^-$ as an example, reactions 15–17 can occur.

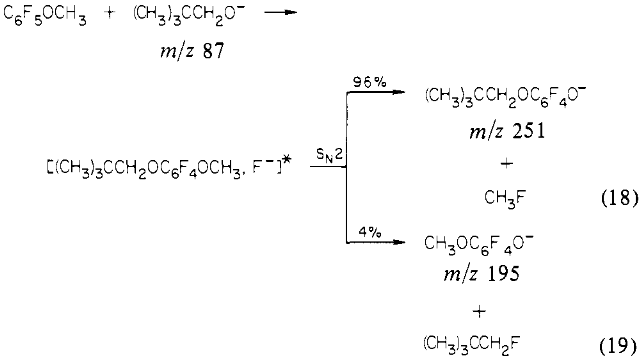


$$\underset{m/z\ 45}{CH_3CH_2O^-} + C_6F_5OCH_3 \longrightarrow [CH_3CH_2OC_6F_4OCH_3, F^-]^* \begin{cases} \xrightarrow{E2} \underset{m/z\ 195}{CH_3OC_6F_4O^-} + C_2H_4 + HF & (15) \\ \xrightarrow{S_N2} \underset{m/z\ 195}{CH_3OC_6F_4O^-} + CH_3CH_2F & (16) \\ \xrightarrow{S_N2} \underset{m/z\ 209}{CH_3CH_2OC_6F_4O^-} + CH_3F & (17) \end{cases}$$

The difference in $\Delta H_f°(CH_3OC_6F_4O^-)$ and $\Delta H_f°(CH_3CH_2OC_6F_4O^-)$ will be nearly the same as the difference between $\Delta H_f°(CH_3F)$ and $\Delta H_f°(CH_3CH_2F)$. This means that the heat of reaction, ΔH_r, will be similar for reactions 16 and 17. The sum of $\Delta H_f°(CH_2CH_2)$ and $\Delta H_f°(HF)$ is 40–45 kJ/mol larger than $\Delta H_f°(CH_3CH_2F)$.[33] This might be taken as an indication of a lower exothermicity of reaction 15 in comparison with reaction 16 or 17. Reaction 15, however, will be favored by entropy.

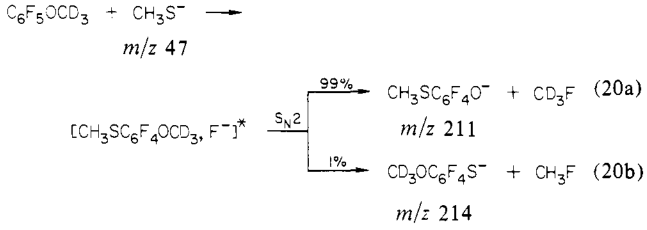
In the $(CH_3)_2CHO^-$ and $(CH_3)_3CO^-$ cases, the number of β-hydrogens is increased. This favors formation of $CH_3OC_6F_4O^-$ relative to $ROC_6F_4O^-$ even more than in the $CH_3CH_2O^-$ system (see Table IV). The formation of $CH_3OC_6F_4O^-$ can easily be accounted for by a facile E2 elimination occurring in the F^- ion–molecule complex. This reaction will probably be less exothermic than the S_N2 substitution on the methyl group. The facility of E2 elimination compared to S_N2 substitutions has also been noted in other systems.[6,34]

Blocking of the E2 elimination channel by using $(CH_3)_3CCH_2O^-$, in which β-hydrogens are lacking, results in nearly exclusive formation of $(CH_3)_3CCH_2OC_6F_4O^-$. S_N2 substitution on the neopentyl group is greatly disfavored relative to S_N2 on the methyl group (eq 18 and 19). Rate constant measurements of the reaction between F^- and neopentyl chloride in the gas phase have revealed a decrease in reaction rate by only a factor of 2 compared to reaction between F^- and methyl chloride.[28] The intramolecular competition between the two S_N2 substitution reactions 18 and 19 seems therefore to reflect more clearly the steric effect of the neopentyl group.[35]



$$C_6F_5OCH_3 + \underset{m/z\ 87}{(CH_3)_3CCH_2O^-} \longrightarrow [(CH_3)_3CCH_2OC_6F_4OCH_3, F^-]^* \xrightarrow{S_N2} \begin{cases} \xrightarrow{96\%} \underset{m/z\ 251}{(CH_3)_3CCH_2OC_6F_4O^-} + CH_3F & (18) \\ \xrightarrow{4\%} \underset{m/z\ 195}{CH_3OC_6F_4O^-} + (CH_3)_3CCH_2F & (19) \end{cases}$$

The sulfur nucleophiles react less efficiently with $C_6F_5OCH_3$ than the oxygen nucleophiles (see Figure 2). On the basis of the principle of hard and soft acids and bases (HSAB),[36] it is expected that the soft sulfur nucleophiles will be less capable of displacing the hard nucleophile F^-. It should, however, also be mentioned that more polarizable anions interact less effectively with electropositive centers in the gas phase.[28] This is reflected in the lower methyl cation affinity of CH_3S^- ($\Delta H_{MCA}(CH_3S^-)$ = 1062 kJ/mol) compared to CH_3O^- ($\Delta H_{MCA}(CH_3O^-)$ = 1130 kJ/mol).[37] Both effects might contribute so as to raise the barrier(s) toward F^- ion–molecule complex formation. Once formed, reactions analogous to those observed for the oxygen nucleophiles occur. The fundamental difference between oxygen and sulfur manifests itself clearly in the competition between the reaction channels available for the internal solvated F^- ion. In the case of reaction between CH_3S^- and $C_6F_5OCD_3$, reattack by F^- occurs nearly exclusively on the methyl group bonded to the oxygen atom (eq 20). Although "symbiotic" behavior between nucleophile and leaving group[36] has been noted in gas-phase systems, it has been concluded to be a moderate effect compared to the methyl cation affinity of the nucleophile.[28] In the present case the methyl carbon atom bonded to oxygen will be more electropositive than the



$$C_6F_5OCD_3 + \underset{m/z\ 47}{CH_3S^-} \longrightarrow [CH_3SC_6F_4OCD_3, F^-]^* \xrightarrow{S_N2} \begin{cases} \xrightarrow{99\%} \underset{m/z\ 211}{CH_3SC_6F_4O^-} + CD_3F & (20a) \\ \xrightarrow{1\%} \underset{m/z\ 214}{CD_3OC_6F_4S^-} + CH_3F & (20b) \end{cases}$$

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(31) $\Delta H_f°(HF)$ = −271.3 kJ/mol, from Benson et al. (Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279–324). $\Delta H_f°(CH_3F)$ = −233.89 kJ/mol, $\Delta H_f°(OH^-)$ = −137.4 kJ/mol, from Rosenstock et al. (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, No. 1). $\Delta H_f°(CH_3O^-)$ = −150.7 kJ/mol, from Bartmess and McIver (Bartmess, J. E.; McIver, R. T. ref 1; Chapter 11, pp 87–121).

(32) The gas-phase ion chemistry of $C_6F_5OCH_2CH_3$ will be described in a following paper; Ingemann, S.; Nibbering, N. M. M., work in progress.

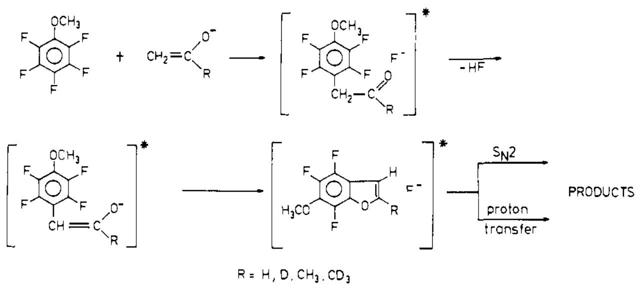
(33) $\Delta H_f°(CH_2CH_2)$ = 52.3 kJ/mol, $\Delta H_f°(HF)$ = −271.3 kJ/mol, and $\Delta H_f°(CH_3CH_2F)$ = −262.0 kJ/mol taken or calculated from the first mentioned reference in ref 31.

(34) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034–5038.

(35) A similar conclusion was reached in King et al. (King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133–7140). Note that in the present case the intramolecular competition is between two mechanistically identical reactions.

(36) Pearson, R. G., Ed. "Hard and Soft Acids and Bases"; Dowden, Hutchinson and Ross, Inc.: Stroudsburg, PA, 1973.

Scheme III



methyl carbon atom bonded to sulfur. The striking selectivity in the reattack by F⁻ might be mainly due to this effect. Even though the detailed underlying reason(s) for the selectivity is uncertain, the result indicates that the higher leaving-group ability of RS groups in solution is a result of solvent effects rather than an intrinsic property.

For the larger thiolate ions the competition between S_N2 substitution and E2 elimination is now different (Table IV). A S_N2 reaction at the *tert*-butyl group can be neglected on the basis of reaction 20a,b, if it occurs at all (eq 21 and 22).

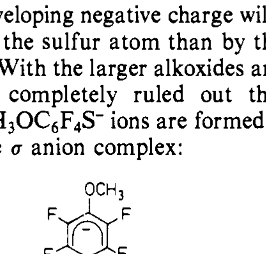
$$C_6F_5OCH_3 + (CH_3)_3CS^- \longrightarrow$$
$$m/z\ 89$$

$$[(CH_3)_3CSC_6F_4OCH_3, F^-]^* \xrightarrow[71\%]{E2} \underset{m/z\ 211}{CH_3OC_6F_4S^-} + HF + (CH_3)_2C{=}CH_2 \qquad (21)$$

$$[(CH_3)_3CSC_6F_4OCH_3, F^-]^* \xrightarrow[29\%]{S_N2} \underset{m/z\ 253}{(CH_3)_3CSC_6F_4O^-} + CH_3F \qquad (22)$$

With the assumption that the internal energy barrier toward S_N2 substitution by F⁻ on the methyl group of the methoxy function will not be influenced drastically by changing the other substituent from $(CH_3)_3CO$ to $(CH_3)_3CS$, then this reaction can be used as an internal standard. The effect of changing the $(CH_3)_3CO$ group, where the reactions corresponding to (21) and (22) occur in the ratio 92:4 (Table IV), to the $(CH_3)_3CS$ group is apparently to raise the height of the local energy barrier toward E2 elimination, thereby rendering it less favored over S_N2 substitution. Although the C–O bond is stronger than the C–S bond, the difference in electronegativity can explain the higher energy barrier; that is, in the transition state of the E2 elimination, the developing negative charge will be less effectively accommodated by the sulfur atom than by the oxygen atom.

With the larger alkoxides and their sulfur analogues, it cannot be completely ruled out that some of the $CH_3OC_6F_4O^-$/$CH_3OC_6F_4S^-$ ions are formed in a more concerted manner from the σ anion complex:



$$\longrightarrow CH_3OC_6F_4Y^- + (CH_3)_2C{=}CH_2 + HF \qquad (23)$$

Y = O, S

A similar mechanism has been proposed to account for the formation of CF_2CFO^- or CH_2CFO^- ions in the reactions between CF_2CF_2[10] or CH_2CF_2[10,14] and alkoxides. In the $C_6F_5OCH_3$ case formation of products arising from reaction by the displaced F⁻ on the original methoxy group can only be explained by formation of a loose F⁻ ion–molecule complex. The fact that S_N2 substitution occurs on the original methoxy group, even though gas-phase E2 eliminations are known to be more facile than S_N2 substitutions, makes it unlikely that a mechanism as the one presented in reaction 23 is operative. The same may be true for the above-mentioned systems composed of RO^-/CF_2CF_2 and RO^-/CH_2CF_2.

Enolate Anions. When the oxygen site in the ambident nucleophiles $CH_2{=}CHO^-$ and $CH_2{=}C(O^-)CH_3$ displace an F⁻ ion from $C_6F_5OCH_3$, an ion–molecule complex composed of an enol ether and F⁻ is formed. For $CH_2{=}CHO^-$ the main product ions are formed by reattack of F⁻ on the neutral in this complex (eq 24 and 25) (Table V). The neutral product in reaction 24 could

$$C_6F_5OCH_3 + CH_2{=}C(R)O^- \longrightarrow$$

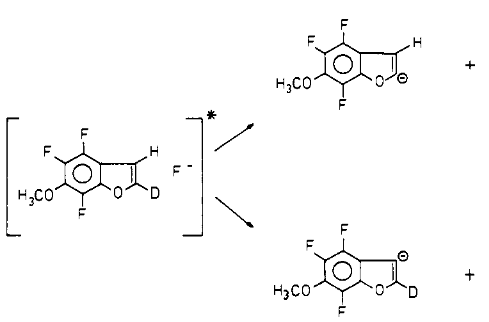
$$[CH_2{=}C(R)OC_6F_4OCH_3, F^-]^* \xrightarrow{E2} \underset{m/z\ 195}{CH_3OC_6F_4O^-} + C_2HR + HF \qquad (24)$$

$$[CH_2{=}C(R)OC_6F_4OCH_3, F^-]^* \xrightarrow{S_N2} CH_2{=}C(R)OC_6F_4O^- + CH_3F \qquad (25)$$

also be $CH_2{=}C(R)F$. This would make the reaction more exothermic by approximately 90 kJ/mol in the case of $CH_2{=}CHO^-$.[38] The carbon atom in the double bond connected to the oxygen atom, however, is not believed to be sufficiently electropositive to undergo nucleophilic attack. The assigned mechanism leading to the $CH_3OC_6F_4O^-$ ion is therefore an E2 elimination. It is somewhat favored over the S_N2 substitution (Table V) for $CH_2{=}CHO^-$, but not as much as in the $CH_3CH_2O^-$ case (Table IV).

The neutral part of the F⁻ ion–molecule complex will contain relatively acidic hydrogens when attack by the carbon site occurs (Scheme III). Proton abstraction to give an enolate ion will therefore be dominant over S_N2 substitution. This situation is analogous to the one in the OH^-, SH^-, $NH_2^-/C_6F_5OCH_3$ systems, and the structure of the ion formed by S_N2 substitution in reaction 25 is believed to be correct. The enolate ion formed in the proton-transfer process is not observed. An intramolecular nucleophilic aromatic substitution leading to a new F⁻ ion–molecule complex takes place (Scheme III). This complex can be described as an F⁻ ion solvated by a substituted benzofuran molecule. The F⁻ ion in this ion–molecule complex reattacks the benzofuran derivative either by proton abstraction or by S_N2 substitution.

The S_N2 and proton-transfer processes are in competition in the $CH_2{=}CHO^-$ system (Table V). Reaction with $CH_2{=}CDO^-$ has revealed that the transferred proton originates two-thirds from the carbon atom next to the oxygen atom and one-third from the other position (eq 26). The structure of the ions formed by reaction 26a,b are probably as shown since ring opening in an elimination type reaction would lead to loss of aromaticity.



+ DF (26a)

+ HF (26b)

Proton transfer is greatly favored over S_N2 substitution in the $CH_2{=}C(O^-)CH_3$ case (Table V). Deuterium labeling shows that the proton abstracted in the final step originates exclusively from the methyl group in the enolate ion. The ion thus formed elim-

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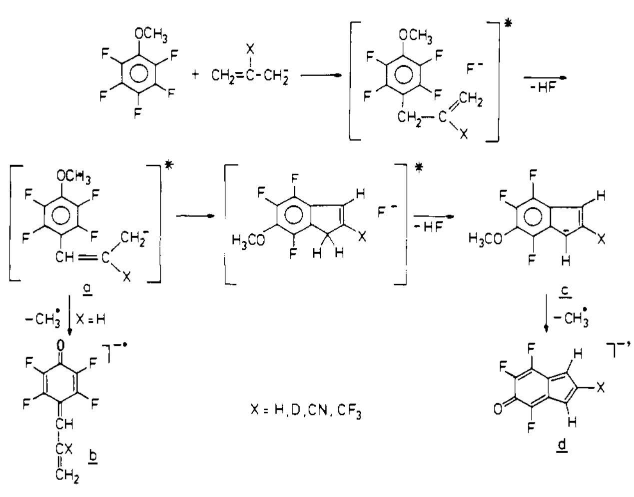
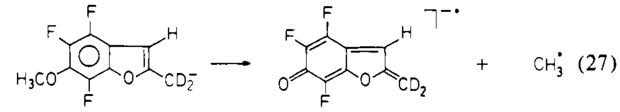
(37) Calculated or taken from Bartmess and McIver (Bartmess, J. E.; McIver, R. T. ref 1; Chapter 11, pp 87–121).

(38) $\Delta H_f°(CH{\equiv}CH) = 54.19$ kJ/mol and $\Delta H_f°(HF) = -271.3$ kJ/mol from the first mentioned reference in ref 31; $\Delta H_f°(CH_2{=}CHF) = -134.8$ kJ/mol from ref 10.

Scheme IV



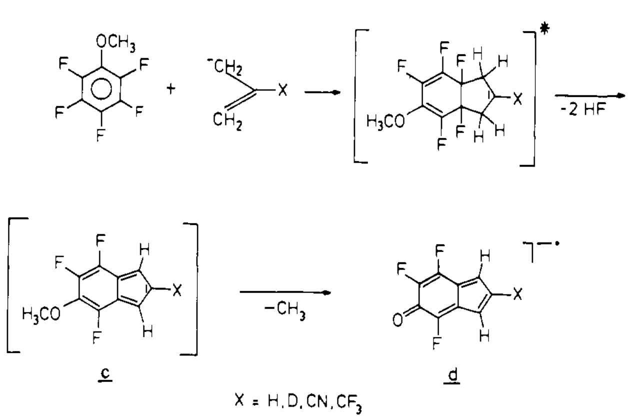
inates a methyl radical to a small extent to give a radical anion, as shown in reaction 27.


(27)

Allyl Anions. Reaction between $C_6F_5OCH_3$ and the enolate anions gives product ions corresponding to loss of 2HF molecules from the collision complex (vide supra). It is evident from the results that this occurs in a stepwise manner involving F^- ion–molecule complexes formed by the displacement reactions. The allyl anion, isoelectronic with the enolate anion of acetaldehyde, can in principle undergo a [2 + 3] or in terms of electrons a [2 + 4] cycloaddition to $C_6F_5OCH_3$ with subsequent loss of 2HF molecules from the cycloadduct (see ref 2 for a discussion on gas-phase anionic cycloaddition). The observed products correspond to loss of HF + $CH_3\cdot$ and 2HF + $CH_3\cdot$ from the collision complex (Table VI). Reaction with specifically labeled allyl anions, where no internal hydrogen/deuterium interchange occurs,[20a,39] proves that the hydrogen atom of the central carbon atom in the allyl anion is not involved in the loss of HF molecule(s). Furthermore, reaction with $CH_2{=}CHCD_2^-$ results in loss of HF + $CH_3\cdot$, DF + $CH_3\cdot$, and HF + DF + $CH_3\cdot$ from the collision complex. These results are consistent with the mechanism proposed in Scheme IV.

The initial displacement reaction leads to an F^- ion–molecule complex, where the neutral contains acidic hydrogen atoms. Proton transfer therefore dominates completely over S_N2 substitution on the methyl group and gives rise to ion a. Part of the ions with structure a can contain sufficient excess internal energy to eliminate a methyl radical and form the observed radical anion b. Another part of the ions with structure a can undergo an intramolecular nucleophilic aromatic substitution in analogy with the enolate anions/$C_6F_5OCH_3$ systems (vide supra). This gives an F^- ion solvated by a highly acidic substituted indene molecule, and proton transfer dominates again over S_N2 substitution. The ring closure followed by the proton abstraction will be a highly exothermic process. Ion c can thereby contain excess internal energy and fragment by loss of a methyl radical to give the observed radical anion d.

Scheme V



Allyl anions having electron-withdrawing groups in the 2-position may be expected to favor the ring-closure reaction after loss of one HF molecule, as these groups then can accommodate the negative charge (Scheme IV). This can explain the absence of ion b in the cases of 2-cyano- and 2-(trifluoromethyl)allyl anions (Table VI). The energy liberated upon ring closure followed by proton transfer will promote the loss of a methyl radical from ion c (observed to a small extent in these cases (Table VI)), thereby leading to ion d, which is the main ionic product observed (Table VI).

The ion at m/z 184 in the allyl anion/$C_6F_5OCH_3$ system and the corresponding product ions formed in reaction with 2-cyano- and 2-(trifluoromethyl)allyl anions could also be rationalized by a synchronous cycloaddition mechanism (Scheme V).

The cycloadduct thus formed may fragment into product ions by loss of 2HF molecules to give the ion c, which can eliminate a methyl radical and form ion d. An argument against this view, however, is found from the loss of HF + $CH_3\cdot$ from the collision complex in the unsubstituted allyl anion case (Scheme IV, Table VI). Nevertheless, it is at present not possible to disregard any of the proposed mechanisms completely when all the observations are taken into account.

Conclusion

Pentafluoroanisole reacts readily with a number of different nucleophiles and appears to be a versatile substrate for studying mechanistic aspects of gas-phase ion–molecule reactions. The observed reactions can all be explained on the basis of a unifying mechanistic picture. The central idea in this picture is that the nucleophilic aromatic substitution process leads to an F^- ion–molecule complex whose lifetime is long enough to allow secondary reactions to take place. The F^- ion–molecule complexes themselves are not observed under the low-pressure conditions used in FT-ICR, but their existence is necessary to explain the obtained results.

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Registry No. $C_6F_5OCH_3$, 389-40-2; HO^-, 14280-30-9; CH_3^-, 3315-60-4; $CH_3CH_2O^-$, 16331-64-9; $(CH_3)_2CHO^-$, 15520-32-8; $(CH_3)_3CO^-$, 16331-65-0; $(CH_3)_3CCH_2O^-$, 55091-58-2; HS^-, 15035-72-0; CH_3S^-, 17302-63-5; $CH_3CH_2S^-$, 20733-13-5; $(CH_3)_3CS^-$, 20733-19-1; NH_2^-, 17655-31-1; $CH_2{=}CHO^-$, 35731-40-9; $CH_2{=}C(CH_3)O^-$, 71695-00-6; $CH_2{=}CHCH_2^-$, 1724-46-5; $CH_2{=}C(CN)CH_2^-$, 83268-51-3; $CH_2{=}C(CF_3)CH_2^-$, 83268-52-4; $O^{-\cdot}$, 14337-01-0; $^{18}O^{-\cdot}$, 36284-90-9; F^-, 16984-48-8.

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[39] Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653.