Isotope labeling experiments conducted with several *n*-propyl iodides confirm that it is the β-hydrogen atoms of the alkyl group which combine with silicon and other alkyls to form the silane products. When hydrogen atoms are added to the system, alkylsilanes form at temperatures <340 K. It appears that the rate-determining process under these conditions is surface diffusion of hydrogen adatoms.

Registry No. Si, 7440-21-3; Al, 7429-90-5; 1-iodopropane, 107-08-4; triisobutylaluminum, 100-99-2; diisobutylsilane, 136425-30-4; isobutene, 115-11-7; isobutylsilane, 18165-87-2; propylene, 115-07-1; dipropylsilane, 871-77-2.

Gas-Phase Ambident Reactivity of Acyclic Enolate Anions

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Abstract: The gas-phase reactions between acyclic enolate anions and unsaturated perfluorocarbon compounds have been studied with use of the method of Fourier transform ion cyclotron resonance. Unsaturated perfluorocarbon compounds react in a characteristic way with either the oxygen or carbon end of an enolate anion to produce distinctive ionic products. The relative yields of ionic products formed in the reactions of a series of ambident acyclic enolate anions of the type $R_1HC{=}CR_2O^-$, reveal the whole spectrum of ambident reactivity from 100% addition via the carbon nucleophilic center up to 99% addition via the oxygen nucleophilic center. There appears to be a correlation between the reaction selectivity and the experimental electron detachment threshold energies, and thus the energy of the HOMO, of the enolate anions. The nature of this correlation suggests that the competition between the reaction channels is controlled by specific frontier orbital interactions of the reactants rather than by the charge distribution in the enolate anions alone.

Ambident ions can be characterized as ions in which reactive sites are connected through mesomerism.[1] The competition between the reactive sites is generally rationalized in terms of orbital versus charge control[2-4] or by making use of the hard and soft concept, which deals with the specific affinities of the atoms which are involved in bond formation.[3,5-7]

Among the ambident ions enolate anions occupy a special position since they play a very important role in synthetic organic chemistry. For this reason considerable effort has been devoted to the controlling factors in the reactions with alkylating agents[1,2,5] such as the influence of the solvent, the temperature, the electrophile, and the counterion.

Most of the charge is thought to be localized on the oxygen atom[4-6,8-10] by which both the solvent and the counterion are favored to associate with this atom[1] thereby shielding it for electrophilic attack. Nonetheless, oxygen alkylation and acylation have been demonstrated to occur in aprotic solvents under conditions where hydrogen bridging and specific solvation of the oxygen were minimized.[1,6]

In order to obtain a better understanding of the intrinsic chemical properties of enolate anions, some research groups have studied enolate anion reactions in the gas phase, where solvent and counterion association is fully eliminated. Under these conditions kinetically favored oxygen alkylation has been found to occur exclusively in the reaction between the enolate anion from cyclohexanone and bromomethane.[11] Yet, it appears from most studies that the gas phase allows a fair competition between the two nucleophilic centers in the enolate anions, in which the properties of both the enolate anion and the substrate seem to play an important role.[12-16]

Gas-phase ion/molecule reactions are typically studied making use of mass spectrometric techniques which in general only allow detection and analysis of the ionic products. Unfortunately, this limitation implies that reaction pathways leading to these product ions cannot be established unambiguously for all reaction systems. Therefore, the reaction between enolate anions and unsaturated polyfluorocarbon compounds is of special interest since it has been demonstrated that addition of oxyanions and carbanions, proceeding via an oxygen[13,15,17-20] and carbon[13,15,21-23] nucleophilic center, respectively, yields distinctive ionic products. On the basis of these probe reactions it has been concluded that in the gas-phase reaction between the acetaldehyde-enolate anion and pentafluoroanisole aromatic substitution proceeds preferentially via oxygen in contrast with the enolate anion of acetone which favors initial addition via carbon.[13] Similarly, the enolate anion of acetic acid is considered to react exclusively via its carbon nucleophilic center with hexafluorobenzene.[24]

Recently, a systematic study has been reported concerning the ambident reactivity of enolate anions in the tube of a flowing afterglow apparatus toward hexafluoropropene.[15] For a series of

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enolate anions derived from aldehydes, ketones, esters, and amides the product ions have been analyzed revealing a range of selectivities spanning from exclusive reaction via the oxygen end up to exclusive reaction via the carbon end of the studied enolate anions. The selectivity has been related to the keto–enol energy differences for the neutral parent carbonyl compounds (ΔH_{ke}). Enolate anions with σ-acceptor or π-donor central substituents (ΔH_{ke} = 40–60 kJ/mol) have been considered to react mainly via oxygen, whereas enolate anions corresponding with larger ΔH_{ke} values (120–160 kJ/mol) have been matched with reactions via carbon. Yet, many enolate anions from both cyclic and acyclic ketones violate the above relationship, of which the chemical nature is still far from clear.

In order to gain understanding a related study has been set up, which is described in the present paper. Under the extremely low pressure conditions in the cell of a Fourier transform ion cyclotron resonance mass spectrometer, the ambident reactivity of a series of acyclic enolate anions toward both hexafluorobenzene and hexafluoropropene has been examined in the absence of thermal interaction between the ion/molecule reaction complex and the environment.

Experimental Section

Experiments were carried out with a homemade Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer[25] equipped with a Bruker 1.4 T electromagnet and a cubic inch cell. General operating and experimental procedures have been described previously.[25] Enolate anions were generated via proton abstraction from the corresponding ketones and aldehydes using primarily generated amide or hydroxide anions as the base. The total pressure was kept typically around 8×10^{-5} Pa. The temperature of the FT-ICR cell was around 330 K as measured by a thermocouple on the trapping plate opposite the filament. The segmented Fourier transform (SEFT) procedure,[26] developed in our laboratory, was used to determine relative ion abundances with an accuracy of better than 1%.

Materials. All chemicals employed were commercially available and were used without further purification. The label content of 1,1,1-trideuterioacetone was better than 93% D_3.[27]

Theoretical Section

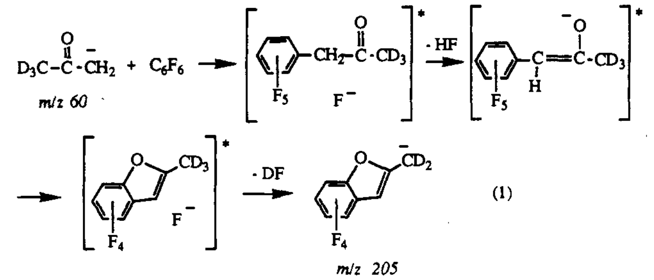
MO energy levels have been calculated for benzene, perfluoropropene, and perfluorobenzene using a density-functional (DF) method as implemented in the Amsterdam DF program system.[28–39] The MOs were expanded in a large set of Slater type orbitals (STOs). The basis is of double-ζ quality (two STOs per nl shell). A 3d polarization function was added on C and F and a 2p polarization function was added to H. Geometries were optimized with a simple Xα exchange-correlation potential[29] using gradient techniques.[37] Imposed point group symmetries are C_s for C_3H_6 and D_{6h} for C_6F_6 and C_6H_6. The data were obtained in the optimum geometry with more sophisticated density-functionals for exchange and correlation.[32–36] The accuracy of the relative DFT MO energy levels can be estimated to be better than 0.1 eV.[39] The absolute MO energies have been obtained by anchoring the calculated energy of the HOMO of benzene to the negative value of its vertical ionization energy, 9.21 eV.[40]

Results

Probe Reactions. As mentioned in the introduction, the reaction between enolate anions and unsaturated polyfluorocarbon compounds is of special interest since it has been demonstrated that addition of oxyanions and carbanions, proceeding via an oxygen[13,15,17–20] and carbon[13,15,21–23] nucleophilic center, respectively, yields distinctive ionic products. Yet, it seems not repetitious to test the course of the reaction via a carbon and oxygen nucleophilic center if these centers are connected through mesomerism such as in enolate anions.

To this end, deprotonated 1,1,1-trideuterioacetone has been reacted with hexafluorobenzene, showing two primary product ions with m/z 205 and 183, respectively.

Formation of the ion with m/z 205 can be rationalized, assuming an addition of the carbon nucleophilic center to the aromatic ring system as depicted in eq 1, resulting in a complex of F^- with the substitution product, which after proton abstraction and subsequent loss of an HF molecule from the complex again results in an enolate anion. This enolate anion undergoes an intramolecular aromatic substitution followed by loss of a DF molecule from the reaction complex leading to the product ion with m/z 205.[41]



(1)

Formation of the product ion with m/z 183 can be associated with addition of the oxygen nucleophilic center in the enolate anion to the aromatic ring, again resulting in a complex of F^- with the substitution product, which after deuteron abstraction and subsequent loss of a DF molecule yields a substituted allyl anion. This allyl anion then loses allene leading to the pentafluorophenoxide anion with m/z 183, as shown by eq 2a.

Alternatively, the substituted allyl anion can undergo an intramolecular aromatic substitution followed by loss of an HF molecule, again yielding a product ion with m/z 205 (eq 2b). Fortunately, this reaction pathway can be excluded, because intramolecular substitution of the asymmetrically deuterium labeled allyl anion would produce the product ion with m/z 205 and the unobserved product ion with m/z 204 (eq 2c) with equal probability, if isotope effects are neglected.[42]

The consistent reactivity pattern described above and the earlier results concerning the reactivity of both carbanions and oxyanions indicate that the product ion distribution in the reaction between enolate anions and hexafluorobenzene or hexafluoropropene can

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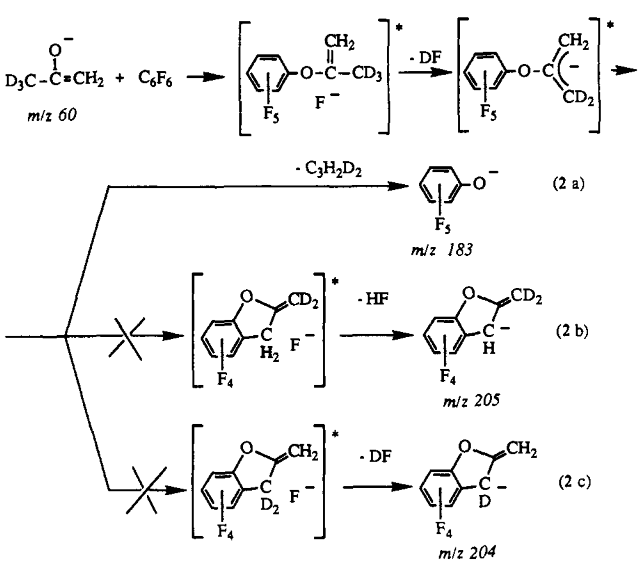
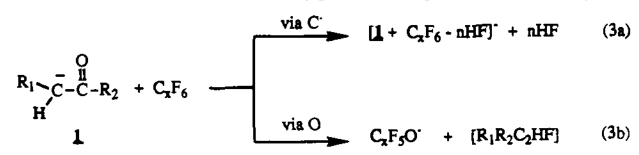
(41) Alternatively, this enolate anion may undergo an intramolecular ipso substitution generating a localized alkene carbanion which may lose propyne resulting in the formation of the $C_6F_5O^-$ ion with m/z 183. On the basis of the estimated difference in heats of formation between $C_6H_5CH{=}C(CH_3)O^-$ and $C_6H_5OC(CH_3){=}CH^-$ (see refs 43 and 40) of about 60 kcal/mol (replacement of the phenyl hydrogens by fluoride will enlarge this difference), the ipso substitution is expected to be highly endothermic and therefore not very competitive. Yet, if this process would slightly contribute to the formation of the ion with m/z 183, the analysis according to eq 3 would slightly overestimate the importance of the reaction channel via the oxygen nucleophilic center of the enolate anion.

(42) Alternatively, the substituted allyl anion may undergo an intramolecular ipso substitution again resulting in an enolate anion. This enolate anion is expected to lose HF or DF with equal probability to generate the ion with m/z 205 or 204, respectively. Since a product ion with m/z 204 is not observed, the process via an intramolecular ipso substitution can also be excluded.



be used as a reliable tool to probe the ambident reactivity of these carbanions, where the yield of [**1** + C_xF_6 − nHF]$^-$ ions represents the relative rate of the reaction via the carbon nucleophilic center (eq 3a), whereas the yield of $C_xF_5O^-$ ions represent the relative rate of the reaction via the oxygen nucleophilic center (eq 3b).

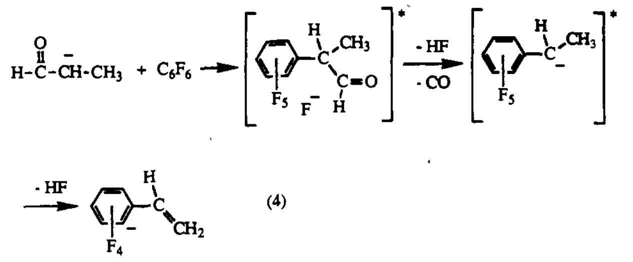


Reaction between $R_1HC{=}CR_2O^-$ and Hexafluorobenzene. The primary product ion distributions in the gas-phase reactions between a series of acyclic enolate anions **1** and hexafluorobenzene have been determined. Following the conclusions of the analysis of the probe reactions, the yield of [**1** + C_6F_6 − nHF]$^-$ ions has been related to the proportion of the reaction course proceeding via addition of the carbon nucleophilic center (eq 3a), whereas the yield of $C_6F_5O^-$ ions has been related to the proportion of the studied reaction course proceeding via addition of the oxygen nucleophilic center (eq 3b).

The enolate anions have been generated by exothermic proton abstraction from the corresponding carbonyl compound (see Experimental Section) which energetically has permitted the production of a mixture of isomeric enolate anions from the methyl ketones (R_2 = CH_3). Because the difference in heats of formation of these isomeric ions is estimated to be about 30 kJ/mol,[40] rationalization of the results obtained for these ions seems ambiguous. Fortunately, the rate constants of the reactions between the delocalized enolate anions and the unsaturated perfluorocarbon compounds are relatively small since it is estimated that less than 30% of the ion–molecule encounter complexes yield products. This allows a rapid proton exchange between the ketones and the enolate anions during which all enolate anions are converted to the most stable $R_1HC{=}C(CH_3)O^-$ reactant ions. The FT-ICR experiments have been set up such that this conversion process toward $R_1HC{=}C(CH_3)O^-$ is completed before the enolate anions have been selected from the reaction mixture and subsequently reacted with the unsaturated fluorocarbon.

The enolate anion from 1,1,1-trifluoroacetone (R_1 = H, R_2 = CF_3) has been found to be the least reactive within the series of enolate anions studied. Unfortunately, the resulting low conversion in the reaction induced by this enolate anion has precluded sufficiently accurate analysis of the product ion distribution.

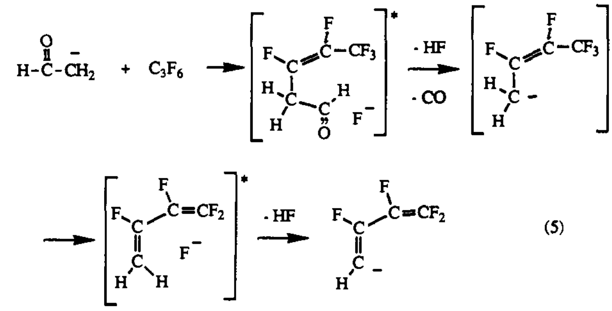
In addition to the common product ions (see eq 3), [**1** + C_6F_6 − nHF − CO]$^-$ product ions have been detected in the reactions of the enolate anions from aldehydes (R_2 = H). Also these product ions have been associated with the reaction via carbon during which in the reaction complex the acidic aldehyde hydrogen is abstracted, followed by loss of an HF and CO molecule as represented in eq 4 for the propionaldehyde–enolate anion. In case of enolate anions from aldehydes containing β-hydrogen (R_1 ≠ H), further elimination of an HF molecule from the remaining benzylic anion has been found to occur (eq 4). The results of the analysis of the product ion distributions in the reactions between **1** and hexafluorobenzene are summarized in Table I.



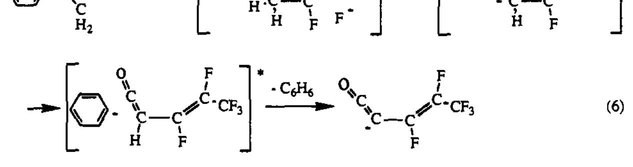
Reaction between $R_1HC{=}CR_2O^-$ and Hexafluoropropene. Following the same procedure as for the reactions with hexafluorobenzene, the primary product ion distributions in the gas-phase reactions between the series of acyclic enolate anions **1** and hexafluoropropene have been determined and analyzed. The results of these analyses are included in Table I.

In general, the overall rate constants of the reactions between **1** and hexafluoropropene have been found to be a factor of about 2 larger relative to the reactions with hexafluorobenzene. As a result, the enhanced conversion in the reaction induced by the least reactive enolate anion within the series, the enolate anion from 1,1,1-trifluoroacetone (R_1 = H, R_2 = CF_3), has made possible a sufficiently accurate analysis of the product ion distribution (see Table I).

Analogous to the reactions with hexafluorobenzene, [**1** + C_3F_6 − nHF − CO]$^-$ product ions have been detected in the reactions of the enolate anions from aldehydes (R_2 = H), which have been associated with the reaction via carbon. In contrast, also in the reaction induced by the enolate anion from acetaldehyde (R_1 = H), loss of HF and CO molecules from the reaction complex has been observed to be followed by the loss of an additional HF molecule. This dissimilarity demonstrates that reaction with hexafluoropropene provides an accessible pathway for the loss of an additional HF molecule as shown in eq 5.



In addition to the common product ions (eqs 3a and 3b), the reaction induced by the enolate anion from acetophenone (R_1 = H, R_2 = C_6H_5) has been observed to give rise to a moderate production of [**1** + C_3F_6 − HF − C_6H_6]$^-$ ions. The formation of these ions can be rationalized by a pathway via initial addition of the carbon nucleophilic center followed by loss of an HF molecule after which the resulting enolate anion eliminates a benzene molecule as shown in eq 6.



It may not be surprising that this type of reaction is unique for the enolate anion from acetophenone, because of all R_2 substituents in the series of **1** studied, the C_6H_5 substituent has the best anion leaving group ability in a base-induced β-elimination reaction.

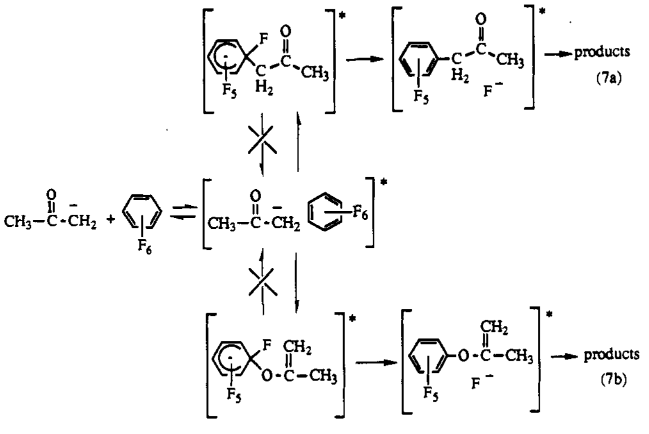
Table I. Oxygen vs Carbon Addition in the Reaction between $R_1HC{=}CR_2O^-$ and C_xF_6

$R_1HC{=}CR_2O^-$		O-/C-addition		electron detachment threshold (eV)
R_1	R_2	C_6F_6	C_3F_6[a]	
H	CF_3	slow reaction	0/100 (0/100)	2.58 ± 0.13[b]
H	F	—	— (2/98)	2.22 ± 0.09[b]
H	$N(CH_3)_2$	1/99	1/99 (5/95)	
H	C_6H_5	6/94	6/94 (2/98)	2.06 ± 0.08[b]
H	$CH{=}CH_2$	30/70	30/70 (32/68)	1.91 ± 0.06[c]
H	$C(CH_3)_3$	—	— (24/76)	1.84 ± 0.07[b]
H	OCH_3	—	— (8/92)	1.80 ± 0.06[b]
H	H	81/19	94/6 (94/6)	1.82 ± 0.02[d]
H	CH_3	19/81	84/16 (87/13)	1.76 ± 0.03[d]
CH_3	CH_3	26/74	82/18	1.67 ± 0.05[b]
CH_3	C_2H_5	26/74	85/15 (80/20)	1.68 ± 0.05[b]
C_2H_5	CH_3	29/71	86/14	
C_3H_7	CH_3	27/73	89/11	
C_4H_9	CH_3	35/65	88/12	
C_5H_{11}	H	95/5	95/5	
C_4H_9	H	91/9	93/7	
C_3H_7	H	86/14	95/5	
C_2H_5	H	84/16	95/5	1.67 ± 0.05[b]
CH_3	H	83/17	97/3 (95/5)	1.61 ± 0.002[d]

[a] Values in parentheses are taken from a flowing afterglow study: see ref 15. [b] See ref 49. [c] See ref 50. [d] See ref 51.

Discussion

The rate-determining step of the addition/elimination process induced by the ambident enolate anions in their reaction with the unsaturated perfluorocarbon compounds can be either the initial addition, generating a σ-complex, or the expulsion of F^- from this initially formed σ-complex. If the expulsion of F^- from the σ-complex is slow relative to the dissociation back to reactants, the observed ratio of oxygen and carbon alkylation would reflect the thermodynamic equilibrium abundance ratio of the corresponding σ-complexes as illustrated in eq 7 for the reaction between the enolate anion from acetone and hexafluorobenzene. This can be expected to result in a very dominant carbon alkylation reaction channel since for all studied enolate anions it can be estimated that the σ-complex leading to carbon alkylation (eq 7a) is at least 100 kJ/mol more stable than the σ-complex leading to oxygen alkylation[43] (eq 7b).



Yet, the results given in Table I show the full spectrum of ambident reactivity within the series of enolate anions studied toward both hexafluorobenzene and hexafluoropropene, suggesting that the initial addition step is irreversible, implying that this step is rate and product determining. Hence, the observed ambident chemical behavior is determined by the relative activation energies for the initial addition via the oxygen and carbon nucleophilic centers of the enolate anions in their reactions with the unsaturated perfluorocarbon compounds.

This is supported by the perfect agreement between earlier results for the reactions between a number of enolate anions and hexafluoropropene obtained under flowing afterglow conditions[15]—included in Table I—and those obtained for the same reactions under the present low-pressure FT-ICR conditions. Evidently, collisional cooling of the intermediate reaction complexes under flowing afterglow conditions, partly resulting in the thermalization of observed reaction complexes, has no influence on the product ion distribution, whereas collision-induced dissociation of these long-lived reaction complexes exhibits identical product ion distributions,[15] again indicating that no thermochemical equilibrium exists within the complex between the σ-complex leading to carbon alkylation and the σ-complex leading to oxygen alkylation. Therefore, one might try to rationalize the influence of the substituents of the enolate anion reaction system on the relative heights of the reaction barriers for the addition via the carbon and oxygen nucleophilic centers.

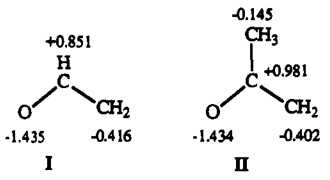


Figure 1. Charge distribution in the enolate anions of acetaldehyde (I) and acetone (II).

In the earlier flowing afterglow study of the gas-phase reactions of hexafluoropropene with a series of enolate anions,[15] the selectivity of the reactions was related with the difference in energies gained upon protonation of the enolate anion on carbon and on oxygen and hence the difference in heats of formation of the keto and enol forms of the neutral carbonyl compounds, ΔH_{ke}. In fact, this relationship suggests that the relative height of the addition reaction barriers is determined by the relative stability of the σ-complex leading to carbon alkylation and the σ-complex leading to oxygen alkylation. Since this thermodynamic argument would favor carbon alkylation for all systems studied, the authors, nevertheless, argued that oxygen alkylation will be favored upon minimizing ΔH_{ke} below 60 kJ/mol. Although the chemical nature of this phenomenon is not yet clear, the empirical relationship was proposed to have predicting capabilities with respect to carbon versus oxygen selectivity, which evidently in the gas phase is determined exclusively by the intrinsic properties of the enolate anion.

Unfortunately, the above empirical relationship is violated by enolate anions of the type $H_2C{=}CR_2O^-$, where $R_2 = CH_2{=}CH$, C_6H_5, *t*-Bu, c-C_3H_5, and CF_3, all with estimated corresponding ΔH_{ke} values below 60 kJ/mol.[43,44] In contrast to the prediction these ions predominantly react via the carbon nucleophilic center.[15] The authors ascribe this aberrant behavior to the possibility that the estimation of the keto–enol energy difference did not adequately account for additional π-conjugation and/or steric effects or to the weak basicity of the enolate anion.[15] Yet, it has been observed in the present study that the enolate anions of the type $R_1HC{=}C(CH_3)O^-$ react dominantly via oxygen with hexafluoropropene, but mainly via carbon with hexafluorobenzene (see Table I).

Clearly, the selectivity is not determined by the intrinsic properties of the enolate anion alone. In this respect, the intrinsic charge distribution in the enolate anion also cannot be exclusively responsible for the observed reaction selectivities.

If the transition states for the addition via oxygen and carbon are dominantly stabilized by electrostatic interactions between the reactants, the addition via the atom accommodating most of the charge is favored. Unfortunately, no experimental data on the charge distributions and MO coefficients of gaseous enolate anions are available, whereas reported theoretical studies are mainly focussed on the heats of formations and the basicity of the anions.[45-50] Yet, it is generally assumed that most of the

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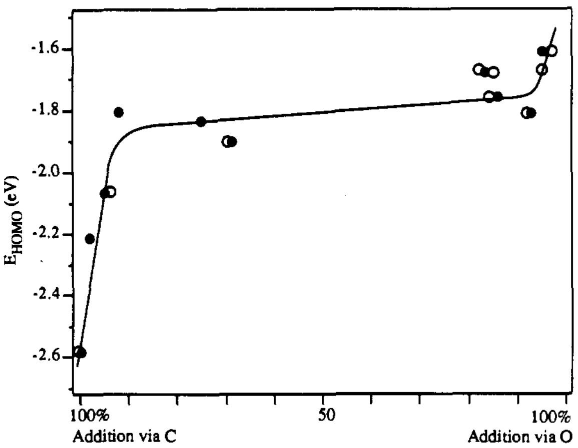

Figure 2. Competition between addition via the carbon and oxygen nucleophilic centers of the enolate anions of the type $R_1HC{=}CR_2O^-$ in the reaction with hexafluoropropene as a function of HOMO energy: (○) values obtained in the present FT-ICR study; (●) values taken from a FA study (see ref 15).

negative charge of enolate anions is carried by the more electronegative oxygen atom.[4-6] This is supported by MO calculations on the enolate anions from acetaldehyde[9] and acetone,[10] which reveal that in both enolate anions the oxygen atom accommodates a total of about −1.43 unit charge, whereas the CH_2 group accommodates a total of about −0.4 unit charge (see Figure 1).

If the competition between the oxygen and carbon nucleophilic centers is exclusively controlled by this charge distribution, both enolate anions are expected to exhibit an identical reaction selectivity where addition of the oxygen nucleophilic center to hexafluorobenzene as well as to hexafluoropropene is dominant. For the enolate anion of acetaldehyde ($R_1 = R_2 = H$) this has been established experimentally (see Table I). However, the enolate anion of acetone ($R_1 = H$, $R_2 = CH_3$) has been found to react dominantly via the oxygen nucleophilic center with hexafluoropropene only, whereas in the reaction with hexafluorobenzene prevalent addition via the carbon nucleophilic center has been observed (see Table I). Moreover, it seems very unlikely that the charge distributions in all the enolate anions, dominantly reacting via the carbon nucleophilic center (see Table I), allow the more electropositive carbon atom to accommodate most of the negative charge. Therefore, it may be obvious that the selectivity of the reaction systems studied is not controlled exclusively by the charge distributions in the enolate anions. This seems to be an intriguing conclusion since coulombic interactions are generally expected to play a very important role in polar reactions in the gas phase in the absence of solvent molecules.

Evidently, the relative activation energy for the addition via the oxygen and carbon nucleophilic centers is determined to a large extent by specific MO interactions. If the enolate anion/unsaturated perfluorocarbon reaction system is considered to be an electron donor/acceptor system, it is expected that the interaction between the HOMO of the enolate anion and the LUMO of the unsaturated fluorocarbon, respectively, dominantly contributes to the stabilization of transition states in the addition reactions.

If, according to the Born–Oppenheimer assumptions, no orbital reorganization occurs during the transition from anion to neutral, the wavelength threshold for photodetachment of an electron is a measure for the energy of the HOMO, E_{HOMO}, of the enolate anion. For a number of enolate anions studied, this experimental wavelength threshold, $E_{h\nu}$, has been reported,[51-53] and these values are included in Table I. In order to reveal the importance of HOMO/LUMO interaction, the individual HOMO energies of the enolate anions ($E_{HOMO} \approx -E_{h\nu}$) have been correlated with the selectivity of the addition reactions. For the reactions between the series of enolate anions and hexafluoropropene, the character of this correlation is illustrated in Figure 2.

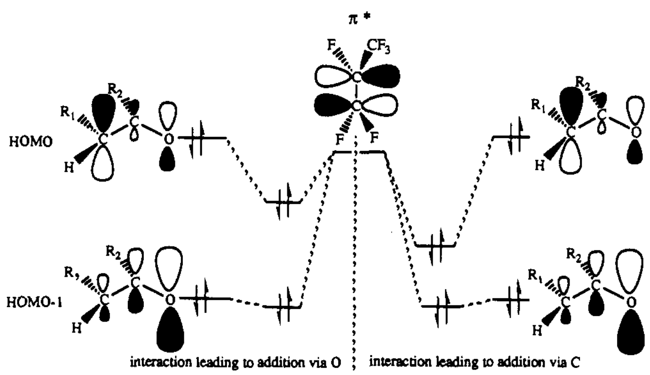

Figure 3. Energy-level diagram for the frontier orbital interactions in the reaction between hexafluoropropene and $R_1HC{=}CR_2O^-$ with a relatively low energy HOMO.

Figure 2 demonstrates that enolate anions with HOMO energies below −1.90 eV dominantly react with hexafluoropropene via the carbon nucleophilic center, whereas above −1.70 eV reaction via the oxygen nucleophilic center is strongly favored. For enolate anions with HOMO energies around −1.80 eV, the competition between the two nucleophilic centers is more balanced.

For the reactions with hexafluorobenzene a similar pattern can be recognized shifted up by 0.10 eV relative to hexafluoropropene, i.e., balanced competition between the carbon and oxygen nucleophilic centers is observed for enolate anions with HOMO energies around −1.70 eV. In this view, the enolate anion from acetaldehyde ($R_1 = R_2 = H$) exhibits an exceptional behavior since its electron photodetachment threshold energy of 1.82 ± 0.02 eV is expected to result in dominant carbon alkylation in contrast with the experimental findings (see Table I). This aberrant behavior may be explained by the possible occurrence of a binding excited state of this enolate anion in the reaction complex which experimentally has been observed to be 1.82 eV above the ground state for the isolated anion.[50,54] To our knowledge, similar excited states have not been reported for other enolate anions.

The correlation between the HOMO energy of the enolate anions and their reaction selectivity demonstrates that specific interactions between the frontier orbitals of the reactants play a very important role. However, the energy gained in these specific interactions can only favorably compete with the energy gained in the assumed strong electrostatic interactions (vide supra) if the energies of the frontier orbitals of the two reactants are very close together. Unfortunately, it is very hazardous to estimate the π LUMO energy of the unsaturated perfluorocarbon compounds from their electron affinities, determined by electron transfer equilibrium measurements or from electron transmission spectroscopy data, because the repulsion resulting from the electron capture will increase the energy of the π-acceptor orbital considerably. Therefore, high-level calculations using density-functional theory (DFT) have been performed (see Theoretical Section) where the MO energy levels have been determined for benzene, perfluoropropene, and perfluorobenzene. The results show that the energy of the lowest unoccupied π orbitals of the hexafluoropropene and hexafluorobenzene, which are involved as the acceptor MO's in the addition of the enolate anions, are

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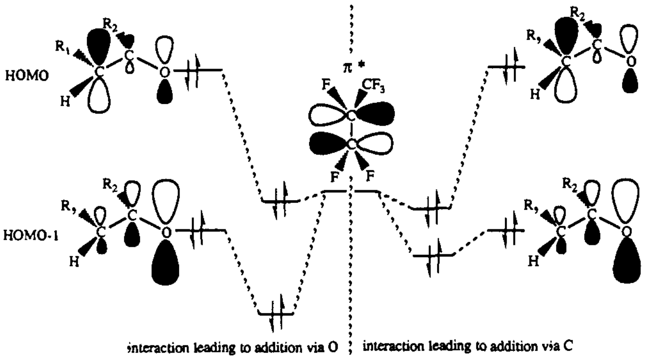

Figure 4. Energy-level diagram for the frontier orbital interactions in the reaction between hexafluoropropene and $R_1HC{=}CR_2O^-$ with a relatively high energy HOMO.

relatively close together: −4.53 and −4.83 eV, respectively. Surprisingly, these energy levels are about 2 eV below the energy levels of the HOMOs of the enolate anions (see Figure 2). However, it may be expected that upon formation of the encounter complex this energy gap will be diminished due to the Coulombic interaction of the anion and the unsaturated fluorocarbon.[29,55]

The above results indicate that the energy levels of the lowest unoccupied π orbital of hexafluoropropene and hexafluorobenzene must be located between the energy levels of the HOMO and HOMO-1 of the enolate anions, which allows a stabilizing interaction with both of these orbitals. Decreasing the HOMO energy of the enolate anion closes the energy gap between the HOMO and opens the energy gap between the HOMO-1 and the lowest unoccupied π orbital of the unsaturated fluorocarbon. This strongly enhances the interaction leading to addition via the carbon nucleophilic center as visualized for the reaction with hexafluoropropene in Figure 3, because the relative orbital coefficient in the HOMO of enolate anions is largest on carbon.[4,8,56]

On the other hand, increasing the HOMO energy of the enolate anions opens the energy gap between the HOMO and closes the energy gap between the HOMO-1 and the lowest unoccupied π orbital of the unsaturated fluorocarbon. This strongly enhances the interaction leading to addition via the oxygen nucleophilic center, as visualized for the reaction with hexafluoropropene in Figure 4, because the relative orbital coefficient in the HOMO-1 of enolate anions is largest on oxygen.[4]

In agreement with the experimental findings (see Figure 1), the above model predicts that enolate anions with a relatively low energy HOMO favor addition to the unsaturated fluorocarbon via the carbon nucleophilic center, whereas enolate anions with a relatively high energy HOMO favor addition to the unsaturated fluorocarbon via the oxygen nucleophilic center. Furthermore, if the above discussed frontier orbital interactions play a leading role in the stabilization of the transition state of the addition reactions, the HOMO energy of the enolate anions reacting with about equal probability via the carbon or oxygen nucleophilic center in their reaction with hexafluoropropene is expected to be relatively close to the HOMO energy of the enolate anions reacting with about equal probability via the carbon or oxygen nucleophilic center in their reaction with hexafluorobenzene, because the lowest unoccupied π orbitals of both unsaturated fluorocarbon compounds are calculated to be very close in energy (vide supra). In accordance with this expectation, the results in Table I indicate that these HOMO energies are less than a few tenths of an electronvolt apart (vide supra). To test the general applicability of the above proposed model a similar study has been conducted on the ambident behavior of cyclic enolate anions which can be considered as a special class of enolate anions with geometric restrictions.[57]

Conclusions

Enolate anions of the type $R_1HC{=}CR_2O^-$ exhibit an ambident chemical behavior in their reaction with both hexafluoropropene and hexafluorobenzene where the competition between the reaction channels involving addition via the carbon and oxygen nucleophilic center of the enolate anions appears to be controlled by specific frontier orbital interactions of the reactants—which are not unprecedented in gas-phase ion/molecule reactions[58]—rather than by the charge distribution in the enolate anions alone. These orbital interactions are assumed to be of a strong electron donor/acceptor type, because the HOMO energy levels of the enolate anions are found to be higher than the energy levels of the lowest unoccupied π orbitals of both unsaturated fluorocarbon compounds.

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Registry No, $CH_2{=}CCF_3O^-$, 136569-07-8; $CH_2{=}CFO^-$, 77213-00-4; $CH_2{=}CN(CH_3)_2O^-$, 136569-08-9; $CH_2{=}CPhO^-$, 34172-40-2; $CH_2{=}C(CH{=}CH_2)O^-$, 125251-12-9; $CH_2{=}CC(CH_3)_3O^-$, 84224-34-0; $CH_2{=}COCH_3O^-$, 136569-09-0; $CH_2{=}CHO^-$, 35731-40-9; $CH_2{=}CCH_3O^-$, 71695-00-6; $CH_3CH{=}CCH_3O^-$, 136569-10-3; $CH_3CH{=}CCH_2CH_3O^-$, 136569-11-4; $CH_3CH_2CH{=}CCH_3O^-$, 136569-12-5; $CH_3(CH_2)_2CH{=}CCH_3O^-$, 136569-13-6; $CH_3(CH_2)_3CH{=}CCH_3O^-$, 136569-14-7; $CH_3(CH_2)_4CH{=}CHO^-$, 136569-15-8; $CH_3(CH_2)_3CH{=}CHO^-$, 136569-16-9; $CH_3(CH_2)_2CH{=}CHO^-$, 136569-17-0; $CH_3CH_2CH{=}CHO^-$, 136569-18-1; $CH_3CH{=}CHO^-$, 77213-03-7; C_3F_6, 116-15-4; CH_3COCF_3, 421-50-1; CH_3COF, 557-99-3; $CH_3CON(CH_3)_2$, 127-19-5; CH_3COPh, 98-86-2; $CH_3COCH{=}CH_2$, 78-94-4; $CH_3COC(CH_3)_3$, 75-97-8; CH_3COOCH_3, 79-20-9; CH_3CHO, 75-07-0; CH_3COCH_3, 67-64-1; $CH_3CH_2COCH_3$, 78-93-3; $CH_3CH_2COCH_2CH_3$, 96-22-0; $CH_3(CH_2)_2COCH_3$, 107-87-9; $CH_3(CH_2)_3COCH_3$, 591-78-6; $CH_3(CH_2)_4COCH_3$, 110-43-0; $CH_3(CH_2)_5CHO$, 111-71-7; $CH_3(CH_2)_4CHO$, 66-25-1; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_2CHO$, 123-72-8; CH_3CH_2CHO, 123-38-6; 1,1,1-trideuterioacetone, 7379-29-5; 1,1,1-trideuterioacetone anion, 136569-06-7; hexafluorobenzene, 392-56-3.

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