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Generation and Chemistry of Fluorinated Acetoxyl and Oxyallyl Biradical Anions (Distonic Radical Anions) in the Gas Phase

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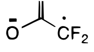
Abstract: Electron impact on fluorinated acetyl compounds $RCOCF_3$ (R = OH, $OSi(CH_3)_3$, OCH_3, CF_3COCH_2, CH_3COCH_2, CH_3, 3,5-$(CF_3)_2C_6H_3CH_2$) in an FT-ICR spectrometer yields ionic products of $m/z = [M - HF]$. These products are proposed to arise via a two-step mechanism: upon electron impact the neutral precursor gives a fluoride ion−neutral radical complex followed by a secondary reaction of the fluoride anion with the neutral radical, either nucleophilic substitution or proton transfer, to yield a biradical anion (distonic radical anion). These radical anions were isolated and their chemical properties were studied. They undergo reactions characteristic of closed-shell anions, *e.g.* proton transfer, or characteristic of open-shell species, *e.g.* radical addition−elimination reactions.

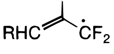
Introduction

Biradical ions (distonic radical ions) are of great interest because they are key intermediates in some reactions,[1−4] they are biologically important,[5] they can be used to study the reactivities of radicals in the gas phase using the charge as a detection tool in mass spectroscopy,[4,6] they have unique chemical properties[4,7−11] which are not seen in conventional radical ions, and they can be used to study the singlet−triplet energy gaps in the corresponding neutral biradicals.[12−14] Although numerous distonic radical anions have been generated using various methods,[8,15−19] there are relatively few published studies of their chemical reactivity in the gas phase.[8−10,20] Most of the previously studied distonic radical anions were formed via oxygen radical anion ($O^{\bullet -}$) abstraction of $H_2^{\bullet +}$ from a neutral precursor.[8,17,21] The products from these reactions are often a mixture of isomers—distonic radical anions and conventional radical anions—with the same *m/z* that are not easily distinguishable by mass spectroscopy.[21] Since the presence of isomeric ions makes chemical studies of distonic radical anions difficult, only a few have been studied successfully using this method (most notably, the distonic 1,4-radical anion of tetramethyleneethane[8]). There are also numerous reports of unimolecularly generated distonic radical anions by techniques such as high kinetic energy collision induced dissociation of anionic precursors,[22−24] but multiple fragments are produced and the distonic radical anion is typically a minor product. Recently, Wenthold and Squires found that distonic radical anions such as *m*- and *p*-benzyne anions and acetate radical anion can be produced by reaction of F_2 with an appropriate trimethylsilyl-containing anion.[9,10] These reactions involve electron transfer to F_2 followed by fluoride-induced desilylation of the radical, and represent a new method for producing pure distonic radical anions. This approach, as the authors note, is limited by the availability of the trimethylsilyl-containing anion precursors[9] and is complicated by the corrosive nature of F_2.

We report here the generation of biradical anions (**1**$^{\bullet -}$−**5**$^{\bullet -}$) unimolecularly from fluorinated precursors. The radical anion is a major product of this simple method. It can be easily isolated, which greatly facilitates its study. Currently, this method appears to be limited to fluorinated compounds. We also present the chemical reactivities of these species in the gas phase. They undergo reactions characteristic of closed-shell anions and characteristic of open-shell radicals.



1$^{\bullet -}$

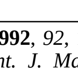


2$^{\bullet -}$ R = CF_3CO

3$^{\bullet -}$ R = CH_3CO

4$^{\bullet -}$ R = H

5$^{\bullet -}$ R =



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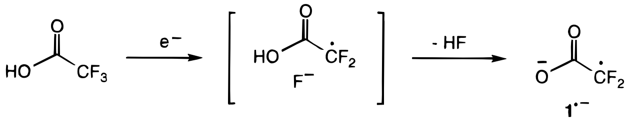
Scheme 1



1a **1b**

Experimental Section

Materials. 3,5-$(CF_3)_2C_6H_3CH_2COCF_3$ was synthesized using Greif's method.[25] 3,5-$(CF_3)_2C_6H_3CH_3$ was synthesized by quenching the Grignard reagent, bis(3,5-trifluoromethyl)benzylmagnesium chloride, with water. All other chemicals were purchased from Aldrich. The neutral samples were used without further purification and were subjected to multiple freeze−pump−thaw cycles before introduction to the cell. There was no evidence of reaction with any impurities.

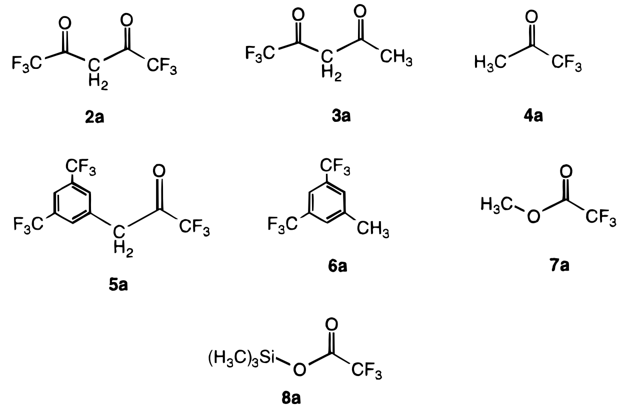
Instrumentation. All experiments were performed with a Fourier Transform IonSpec OMEGA ion cyclotron resonance (FT-ICR) spectrometer (2 in. cubic cell) equipped with impulse excitation.[26,27] Neutral samples were admitted to the high-vacuum can by means of Varian leak valves. All ions were trapped in a magnetic field in the range 0.6−0.7 T. The kinetic energy of the incident electrons was controlled by varying the potential applied to a rhenium filament and the bias on the trapping plates. The operating current of the filament was about 2.2 A and the electron energy necessary to produce the radical anions ranged from 2.8 to 20 eV. For subsequent studies of the reactivity of the radical anions, all other ions were ejected by standard double-resonance techniques. The typical operating pressures were 3-8 × 10^{-7} Torr. All experiments were conducted at ambient temperature estimated to be 350 K.[26]

Results

Generation of the Biradical Anions. Electron impact (2.8 eV) on CF_3COOH (**1a**) affords two product ions: $[M - HF]^-$ ($m/z = 94$) and $[M - H]^-$ ($m/z = 113$). Analysis of the appearance of these ions indicates that $[M - HF]^-$ is formed initially by electron impact, while $[M - HF]^-$ is formed as a secondary proton transfer product (discussed later). We propose that the product $[M - HF]^-$ is the biradical anion $\mathbf{1}^{\bullet-}$, formed by the mechanism shown in Scheme 1.

Electron impact on the precursor **1a** produces the fluoride−radical complex **1b**. Subsequent deprotonation of the neutral radical by fluoride prior to dissociation yields the radical anion $\mathbf{1}^{\bullet-}$. This mechanism is supported by the observation that electron impact on the fluorinated ketones **2a**−**5a** gives the corresponding radical anions ($\mathbf{2}^{\bullet-}$−$\mathbf{5}^{\bullet-}$). In all cases other than **5a**, the loss of HF must comprise loss of a proton and a fluorine from two separate carbons at the α position of the carbonyl group. In case of **3a**, there are two kinds of acidic hydrogens which can be abstracted by fluoride, and both pathways will produce a biradical anion. The product $\mathbf{3}^{\bullet-}$ is thermodynamically more favorable, and therefore we believe that it is the more likely product. We believe that generation of $\mathbf{5}^{\bullet-}$ proceeds through the same mechanism as **2a**−**4a** because electron impact on **6a** does not generate any measurable ion signal. The negative result for **6a** suggests that either the mechanism described above is sensitive to the nature of the C−F bond being cleaved or the subsequent proton transfer is not efficient. The former is more likely, since we observe that the proton transfer between F^- and **6a** is fast. Once generated, the intermediate complex can undergo chemical transformations other than proton transfer when such pathways are thermodynamically and kinetically accessible. For example, the radical anion $\mathbf{1}^{\bullet-}$ can also be generated by electron impact on both methyl trifluoroacetate (**7a**) and trimethylsilyl trifluoroacetate (**8a**). After the fluoride−radical complex is produced by electron impact, a subsequent nucleophilic substitution reaction of fluoride at either the methyl or the trimethylsilyl group produces the radical anion.

Chart 1



2a **3a** **4a** **5a** **6a** **7a** **8a**

We propose that the products from electron impact on these precursors are biradical anions ($\mathbf{1}^{\bullet-}$−$\mathbf{5}^{\bullet-}$) because of the chemistry they exhibit (see below) and because this is the most likely path for the neutral precursors to lose HF upon electron impact producing radical anions. The rearrangement of the biradical anions ($\mathbf{2}^{\bullet-}$−$\mathbf{5}^{\bullet-}$) through internal 1,3 H-shifts is unlikely since the product is much less stable. The biradical anions ($\mathbf{1}^{\bullet-}$−$\mathbf{5}^{\bullet-}$) represent an interesting class of distonic radical anions, because the charge and the spin may be delocalized through the conjugated π system (see Discussion for detail). Examples of similar biradical anions, such as tetramethyleneethane,[8] $^{\bullet}CH_2CO_2^-$,[10] trimethylenemethane, and *m*- and *p*-benzyne,[9] have been previously reported.

Chemical Reactivity. The radical anions described above were generated unimolecularly in the FT-ICR and were readily isolated by ejecting all other ions. This enabled us to study the reactivity of these species with a wide variety of neutral reactants. The anion $\mathbf{5}^{\bullet-}$ was chosen for extended reactivity studies because it is most easily generated. The ionic products between $\mathbf{5}^{\bullet-}$ and various neutral substrates are listed in Table 1.

Squires and co-workers[9,10] have examined the reactions of the distonic radical anion $^{\bullet}CH_2CO_2^-$ with SO_2 and NO_2 and observed $CH_2^{\bullet-}$ transfer to each of these substrates. We find that $^{\bullet}CF_2CO_2^-$ gives $CF_2^{\bullet-}$ transfer with SO_2 but not with NO_2.

$$^{\bullet}CF_2CO_2^- + SO_2 \longrightarrow {}^{\bullet}CF_2SO_2^- + CO_2$$

In contrast to distonic radical cations, which react with $CH_3S{-}SCH_3$ and $CH_3Se{-}SeCH_3$,[4,7] no reaction was observed between each of the biradical anions ($\mathbf{1}^{\bullet-}$−$\mathbf{5}^{\bullet-}$) and these two substrates. Similarly, other known distonic radical anions such as the distonic 1,4-radical anion of tetramethyleneethane are not observed to react with $CH_3S{-}SCH_3$,[8] although $^{\bullet}CH_2CO_2^-$ reacts slowly with $CH_3S{-}SCH_3$.[10]

Discussion

Similar to distonic radical cations, the chemical reactivities observed for radical anions ($\mathbf{1}^{\bullet-}$−$\mathbf{5}^{\bullet-}$) can be categorized into two kinds of behaviors. First, they behave like closed-shell

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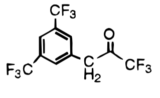
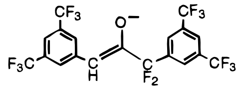
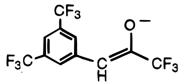
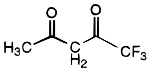
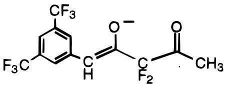
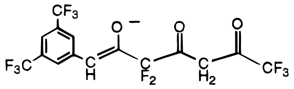
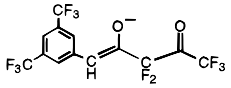
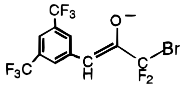
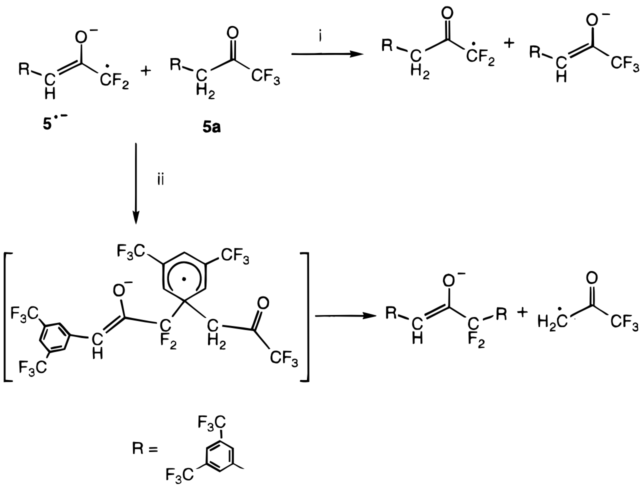
Table 1. Reactions of **5**$^{\bullet-}$ with Various Neutral Substrates

Neutral Substrates	Ionic Products and their distributions	
 **5a**		30%
		70%
 **3a**		49.7%
		34.7%
		15.6%
Br_2	$Br_2^{\bullet-}$	65.6%
	Br^-	27.5%
		6.9%

Scheme 2

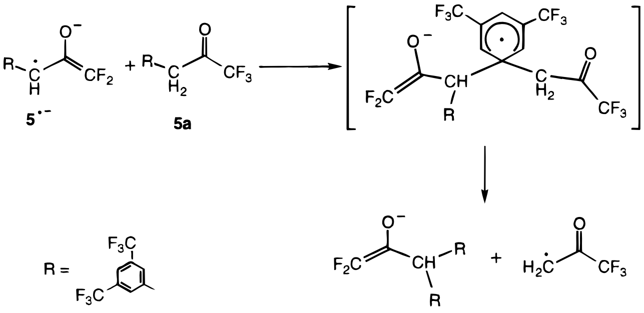


i = proton transfer; ii = radical addition-elimination

anions. For example, in the reaction of **5**$^{\bullet-}$ with **5a**, the proton transfer product $[3,5\text{-}(CF_3)_2C_6H_3CHCOCF_3]^-$ was observed (Scheme 2, path i). The reaction is less than unit efficient, similar to that observed for the proton transfer between enolates and ketones.[28] If F atom transfer from **5a** to **5**$^{\bullet-}$ occurs, the products are indistinguishable from the proton transfer reaction. In order to exclude this possibility, we studied the reaction between **5**$^{\bullet-}$ and **2a** by keeping the pressure of **5a** so low that the reaction between **5**$^{\bullet-}$ and **5a** is insignificant. In this reaction, proton transfer and F atom transfer lead to different anionic products; only the product corresponding to proton transfer was observed.

We also observe reactivity that cannot be explained by the conventional reactions of closed-shell enolate anions, but that is consistent with reactions of radicals. The observation of several products, such as [**5**$^{\bullet-}$ + $(3,5\text{-}(CF_3)_2C_6H_3)$], [**5**$^{\bullet-}$ + $COCH_3$], [**5**$^{\bullet-}$ + $COCF_3$], and [**5**$^{\bullet-}$ + $COCH_2COCH_3$] shown in Table 1, can be attributed to radical addition–elimination mechanisms. Similar radical reactions have been observed for distonic radical cations in the gas phase.[29,30] The reaction between **5**$^{\bullet-}$ and **5a**, for example, produces an anion of *m/z* corresponding to [**5**$^{\bullet-}$ + $(3,5\text{-}(CF_3)_2C_6H_3)$] in addition to the proton transfer product described earlier. Since both the proton transfer product and the radical addition–elimination reaction product were observed (see Table 1), the radical addition is fast enough to compete with the ionic proton transfer reaction. A simple mechanism for formation of the product [**5**$^{\bullet-}$ + $(3,5\text{-}(CF_3)_2C_6H_3)$] involves radical addition to the benzene ring of **5a** to yield the carbon-centered radical intermediate of Scheme 2, path ii. This intermediate may eliminate the radical anion **5**$^{\bullet-}$ to generate the reactants, or it may eliminate the radical $^{\bullet}CH_2COCF_3$ which leaves a closed-shell anionic product of the observed *m/z*.

Scheme 3



There is another possible pathway in which the CH group, rather than the CF_2 group, acts as a carbon radical (Scheme 3). In this case, CH group addition to the benzene ring gives the same mass ionic product as the mechanism in Scheme 2, path ii, but this is less likely because of the following: (a) the product [**5**$^{\bullet-}$ + $(3,5\text{-}(CF_3)_2C_6H_3)$] can be isolated and it does not react with **5a** via a proton transfer reaction (if the product is from this pathway, its structure would be $RRCHCOCF_2^-$ (Scheme 3), and proton transfer from **5a** should be observed since **5a** is more acidic than $RRCHCOCF_2{-}H$ by about 15 kcal/mol);[31] and (b) the product from this pathway is less stable since the charge cannot be stablized by the benzene ring.

A similar mechanism accounts for the products formed in the reaction of **5**$^{\bullet-}$ with **3a**, in which initial radical addition occurs at either of the two carbonyl groups (Scheme 4). Each of the intermediates may then eliminate a radical to give either of two ionic products. We observe ionic products whose *m/z* ratios correspond to three of the four possible radical addition–elimination products. Products from the radical addition at the acetyl carbonyl have higher yields than those from the radical addition at the trifluoroacetyl carbonyl (the ratio of these two pathways is about 6:1, see Table 1). This is consistent with the well-documented observation that radicals having electron-attracting groups react preferentially with double bonds having electron-releasing substituents.[32] The product distributions in

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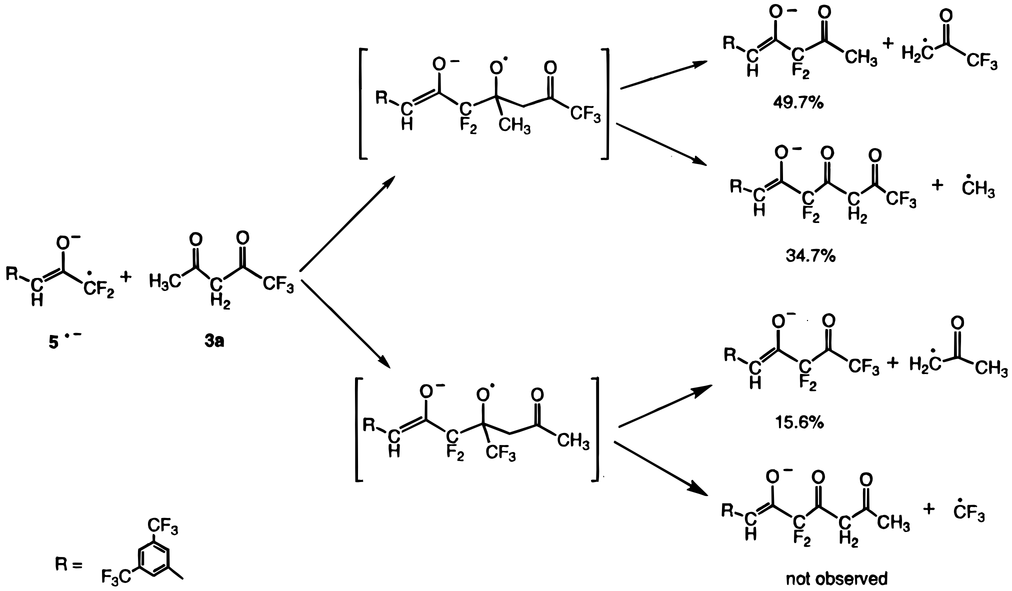
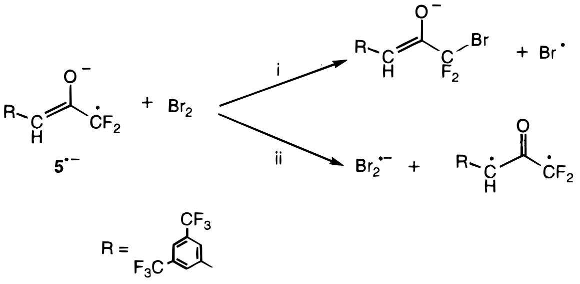
Scheme 4



Scheme 5

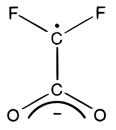


i = radical abstraction; ii = electron transfer.

this reaction also support the radical mechanism instead of one involving initial anionic addition to the carbonyl; anionic addition should take place preferentially at the CF_3CO group.

In addition, in the reaction of **5**$^{\bullet-}$ with Br_2, we observe a radical abstraction reaction giving $[M + Br]^-$ (Scheme 5, path i), and electron transfer from **5**$^{\bullet-}$ to Br_2 producing $Br_2^{\bullet-}$ and the corresponding biradical **5**$^{2\bullet}$ (Scheme 5, path ii). Thus the electron affinity of the biradical **5**$^{2\bullet}$ is less than 2.4 eV, the electron affinity of Br_2. The radical abstraction reaction is somewhat slower than the electron transfer; the ratio of $Br_2^{\bullet-}$ to $[M + Br]^-$ is about 10:1.[33]

The chemical reactivity described above supports the conclusion that **1**$^{\bullet-}$–**5**$^{\bullet-}$ are biradical anions. In these radical anions, the charge and the spin can be delocalized through the conjugated π system. In order to better understand the electronic structures of these species, we have performed *ab initio* MO calculations on **1**$^{\bullet-}$ and **4**$^{\bullet-}$.[34,35] For the radical anion **1**$^{\bullet-}$, a Mulliken population analysis shows that the charge is mainly delocalized on the two carboxylate oxygen atoms and that most of the spin density is on the CF_2 carbon. This can be easily understood from an examination of the HOMO and HOMO-1 of **1**$^{\bullet-}$ shown in Figure 1. The p orbitals of the oxygen atoms make the largest contribution to the HOMO-1 and the p orbitals of the CF_2 group make the largest contribution to the HOMO. Therefore, this radical anion mostly looks like a carboxylate anion and a carbon radical (Figure 1).



1$^{\bullet-}$

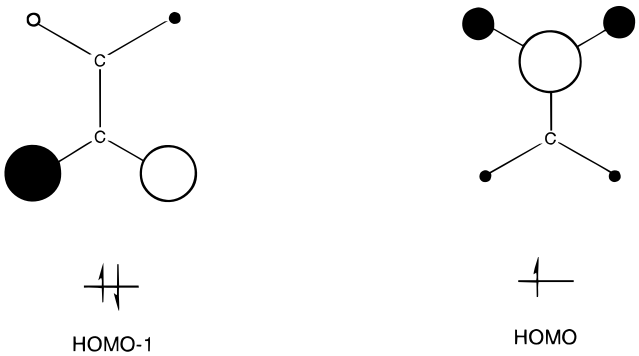


Figure 1. The HOMO and HOMO-1 of **1**$^{\bullet-}$ from the *ab initio* calculation. Only the top lobes of the p orbitals are shown.

In the case of radical anion **4**$^{\bullet-}$, the charge and the spin delocalize over the whole molecule. Due to the high electronegativity of the oxygen atom, the charge is mostly on the oxygen atom with some charge on the CH_2 and CF_2 groups. Most of the spin is delocalized on the two carbons of CF_2 and CH_2. We expect the other radical anions to also exhibit electronic structures similar to that of **4**$^{\bullet-}$.

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[33] We observed a third product, Br^-, which can be produced from multiple pathways such as: dissociation of $Br_2^{\bullet-}$, radical abstraction followed by electron transfer, and an S_N2-type reaction between **5**$^{\bullet-}$ and Br_2.

[34] **1**$^{\bullet-}$ and **4**$^{\bullet-}$ were chosen since they were the smallest molecules in the study. Geometries were optimized at the UHF/6-31+G* level of theory using Gaussian94. Vibrational frequencies were calculated to ensure that the geometries obtained are minima on the potential energy surface.

[35] Gaussian 94, Revision C.3; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; M. Challacombe; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995

Summary

We have described a simple method of generating various gas-phase biradical anions unimolecularly in an FT-ICR spectrometer. We have conducted studies on the unique chemical properties of these interesting species. We observe that they can react like either ions (*e.g.*, proton transfer reaction) or radicals (*e.g.*, radical addition−elimination and radical abstraction). Radical addition−elimination reactions are observed with both a benzene ring (reaction between $\mathbf{5}^{\bullet-}$ and **5a**) and carbonyl groups (reaction between $\mathbf{5}^{\bullet-}$ and **3a**). The selectivity of the radical in the reaction of $\mathbf{5}^{\bullet-}$ with **3a** can be understood from the fact that radicals having electron-attracting groups react preferentially with double bonds having electron-releasing substituents.[32]

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