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Gas-phase negative ion chemistry of molecular fluorine. Synthesis of distonic radical anions and related species

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Abstract

The gas-phase negative ion chemistry of molecular fluorine is described, with an emphasis on its use in the regiospecific synthesis of distonic radical anions and related species. Sequential reaction of organic compounds containing two trimethylsilyl (TMS) substituents with F^- followed by F_2 produces distonic radical anions with the negatively charged and odd-spin sites determined by the locations of the TMS groups. The mechanism of the F_2 reaction involves dissociative electron transfer from the TMS-substituted carbanion to F_2, yielding an F^-/radical complex; subsequent attack by F^- on the TMS group of the radical produces the distonic radical anion product. Experimental evidence in support of the proposed mechanism is presented, including the dependence of the efficiency of radical anion formation on both the electron binding energy of the reactant carbanion and the leaving-group ability of the radical anion product. Selected applications of the F_2 method for distonic anion synthesis are described, including formation of the negative ions of trimethylene methane, the benzynes, oxyallyl and acetoxyl biradicals and α,3-dehydrotoluene. Mechanistic variations in the F_2 reactions with carbanions are described in which the transient F^- ion produced by dissociative electron transfer to F_2 reacts with the organic radical in the long-lived complex by proton transfer, nucleophilic substitution at carbon, and elimination. Formation of distonic biradical anions (ionized triradicals) from neutral precursors containing three TMS groups is described, along with the rational gas-phase synthesis using F_2 of distonic carbene and nitrene anions. (Int J Mass Spectrom 179/180 (1998) 173–183) © 1998 Elsevier Science B.V.

Keywords: Molecular fluorine; Distonic radical ion; Negative ion; Ion/molecule reaction; Flowing afterglow

1. Introduction

Burgeoning interests in the properties and reactivity of distonic radical ions [1] have motivated the development of new gas-phase synthetic approaches to these species. Distonic radical cations have been generated for chemical and physical studies by electron-impact ionization of selected neutral compounds [1,2], by ion/molecule reactions [1,3], and by collision-induced and photoinduced dissociation of selected precursor ions [4]. Ion/molecule reactions are the most common method for generating distonic radical anions [1], although syntheses based upon dissociative ionization have also been described [5]. One of the most widely used ion/molecule reactions is 1, n ($n = 2,3,4 \ldots$) abstraction of $H_2^{\cdot +}$ from neutral organic compounds by atomic oxygen anion [6]. This

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Dedicated to Professor Fulvio Cacace in recognition of his 40 years of seminal contributions to gas-phase ion chemistry.

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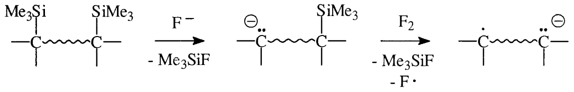
approach has been used to produce a variety of different distonic radical anions, including *o*-benzyne anion from benzene [7], tetramethyleneethane (TME) anion from 2,3-dimethyl-1,3-butadiene [8], methylenethiocyanomethyl anion $[CH_2SCHCN]^{\cdot -}$ from methylthioacetonitrile [9], 1,2-cubene anion from cubane [10], and 2,4-dimethylenecyclobutane-1,3-diyl anion from 1,3-dimethylenecyclobutane [11]. Although this synthetic method has provided several important distonic radical anions for chemical studies, it lacks generality because the mode of $H_2^{\cdot +}$ abstraction is uncontrollable, often unpredictable, and it sometimes fails altogether. For example, $O^{\cdot -}$ reacts with 2-methylpropene to give only OH^- instead of the desired trimethylenemethane (TMM) anion which might have formed by a 1,3-$H_2^{\cdot +}$ abstraction [8]. Similarly, propene, allene, propyne, and halobenzenes all react with $O^{\cdot -}$ to give complicated mixtures of 1,*n*-$H_2^{\cdot +}$ abstraction products, among others [6, 12]. Sometimes these product mixtures can be resolved through the use of deuterium-labeled neutral precursors [7,8,13]. However, recent work in our laboratory with other deuterated hydrocarbons has shown that the relative yields of $H_2^{\cdot +}$, $HD^{\cdot +}$, and $D_2^{\cdot +}$ abstraction are not necessarily reliable indicators of the isomeric product distribution, because H/D exchange between the nascent radical anion and the water molecule can occur within the ion/molecule complex prior to dissociation [14].

We sought an alternative method for synthesizing distonic radical anions in a regiospecific manner with absolute ion yields that were suitable not only for ion/molecule reaction studies, but also for subsequent investigation by negative ion photoelectron spectroscopy (NIPES). NIPES experiments require substantial currents (10–100 pA) of structurally defined negative ions for determining the electron affinity and electronic state energy splittings of the corresponding neutral species [15]. The broad applicability of the fluoride-induced desilylation procedures developed by DePuy and co-workers for regiospecific synthesis of gas-phase carbanions [16] inspired us to examine the possibilities for "double desilylation" of *bis*-trimethylsilyl compounds, wherein the two trimethylsilyl groups would determine the positions of the charged and odd-spin sites in the radical anion products. Using this strategy, we recently developed a stepwise synthetic procedure for generating gas-phase distonic radical anions by first forming a trimethylsilyl-containing carbanion from the corresponding *bis*-trimethylsilyl precursor using the DePuy procedure, and then allowing this ion to react with *molecular fluorine*, F_2, in order to effect the displacement of the remaining trimethylsilyl group:



(1)

A brief account of this ion synthesis method and its application to the formation of TMM radical anion and the isomeric benzyne radical anions has been published [17]. Additional details of the benzyne radical anion syntheses have been reported [18, 19], as well as further applications of the method to the generation of acetate radical anion [20], distonic *biradical* anions (ionized triradicals) [21], and distonic *carbene* anions (charged carbenes) [22]. This ion synthesis has also been used for photoelectron spectroscopy studies of TMM [23] and the benzynes [24], and for neutralization-reionization (NRMS) studies of acetoxyl biradical [25]. In this article we outline the scope and flexibility of this radical anion synthesis procedure, and we examine some of the mechanistic details involved in the reactions of F_2 with gaseous carbanions.

2. Experimental

All of the experiments described in this article were carried out at room temperature (298 ± 2 K) in a flowing afterglow-triple quadrupole instrument that has been described previously [26]. Helium buffer gas was maintained in the 1 m × 7.3 cm flow reactor at a total pressure of 0.4 Torr, with a flow rate of 200 STP cm^3/s and bulk flow velocity of 9700 cm/s. Primary reactant ions such as F^- and OH^- are produced by electron impact ionization of NF_3 and a N_2O/CH_4

mixture, respectively, which are added near the electron emission source located at the upstream end of the flow tube. Ions generated in this manner are transported down the tube by the flowing helium, where they are allowed to react with gaseous neutral reagents introduced through metered inlets. The ions produced in the flow tube are thermalized to ambient temperature by $\sim 10^5$ collisions with the helium buffer gas. The negative ions in the flowing plasma are extracted from the flow tube through a 0.5 mm orifice in the nose cone, and then focused into a triple quadrupole analyzer for either single-stage or tandem mass spectrometric analysis. For collision-induced dissociation (CID) experiments, collision energies of 15–20 eV (lab) were used with argon target gas pressure of 0.05–0.08 mTorr in the quadrupole collision cell (Q2). The product ions and unreacted parent ion are extracted from Q2 with an electrostatic lens into the third quadrupole, where they are mass analyzed and then detected with an electron multiplier operated in pulse counting mode.

2.1. Materials

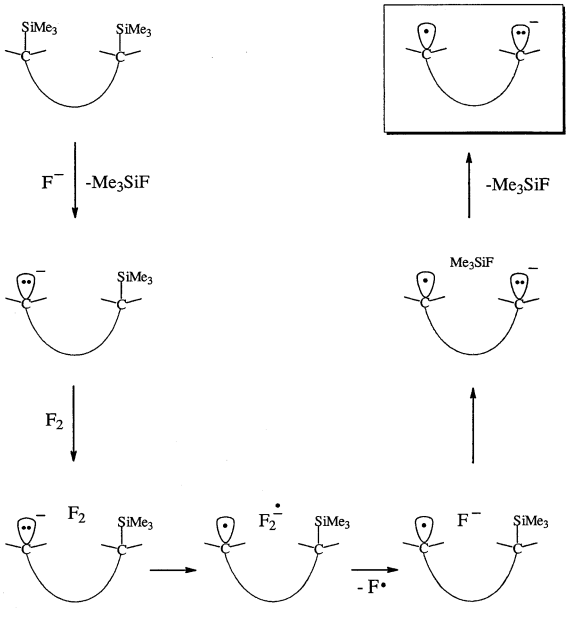
The *mono*-, *bis*-, and *tris*-trimethylsilyl compounds were prepared by standard methods described in our previous work. All other reagents were obtained from commercial sources and were used as supplied except for degassing just prior to use. Gas purities were as follows: He (99.995%), F_2 (5% in He), NF_3 (98%), CH_4 (99%), N_2O (99.5%).

3. Results and discussion

The synthesis of distonic radical anions from *bis*-trimethylsilyl compounds is a two-step procedure in which the neutral precursor is first reacted with F^- in the upstream portion of the flow tube, followed by reaction of the resulting carbanion with F_2 added further downstream as a dilute mixture in helium. In order to facilitate discussion, we present in Table 1 (TMS = $SiMe_3$) a listing of radical anions and related species that have been formed by this method, along with the corresponding neutral precursors and carbanion intermediates. We first discuss the mechanism of the reaction of F_2 with TMS-substituted carbanions, and then outline several variations on the ion synthesis procedure that significantly extend its scope and utility.

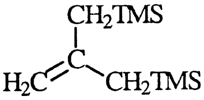
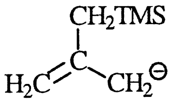
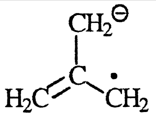
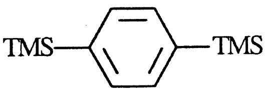
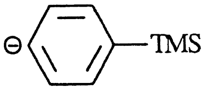
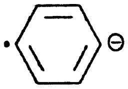
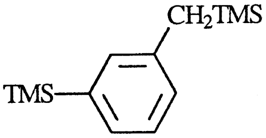
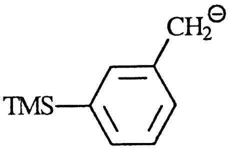
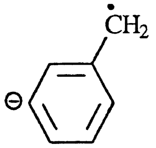
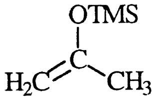
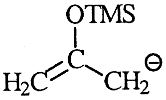
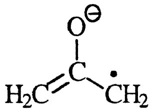
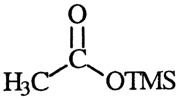
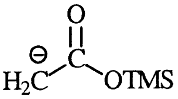
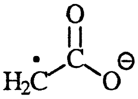
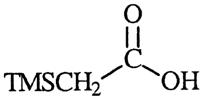
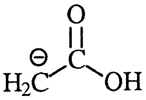
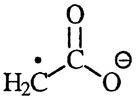
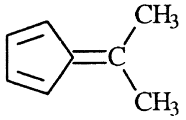
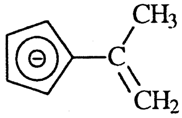
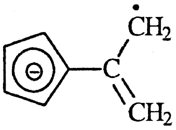
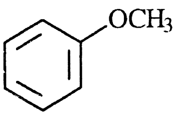
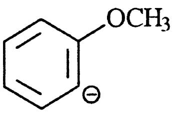
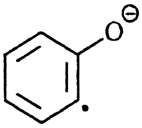
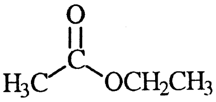
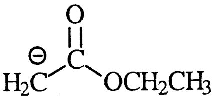
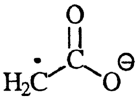
3.1. Mechanism of the F_2 reaction

The general mechanism outlined in Scheme 1 can be divided into three key steps: (i) formation of the initial carbanion reactant, (ii) dissociative electron transfer from the carbanion to F_2 within the ion/molecule collision complex forming F^- and an organic radical, iii) nucleophilic attack by F^- on the trimethylsilyl group of the radical to produce the distonic radical anion. For example, consider the formation of TMM radical anion **1** from the *bis*-trimethylsilylbutene precursor (Table 1, entry 1). Fluoride-induced desilylation produces the 2-trimethylsilylmethylallyl carbanion regiospecifically [16]. Reaction with F_2 proceeds by electron transfer in the collision complex forming $F_2^{\cdot -}$ and a TMS-substituted allylic radical. The electron affinity of F_2 is 71 kcal/mol [27], whereas the EA of the allylic radical is



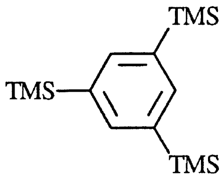
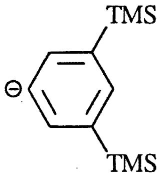
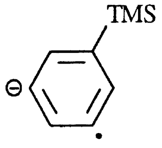
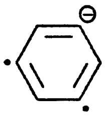
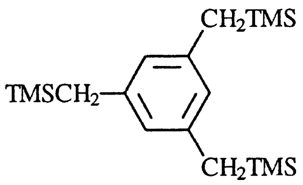
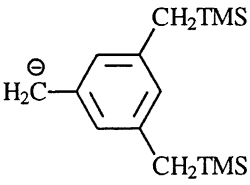
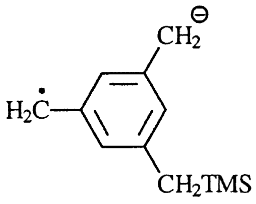
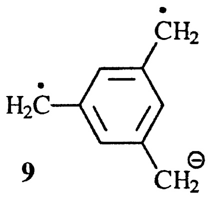
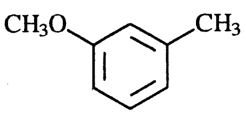
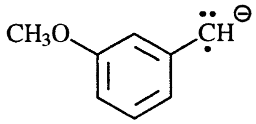
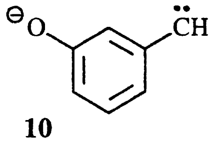
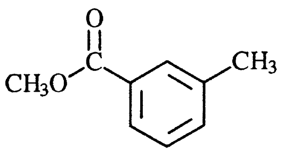
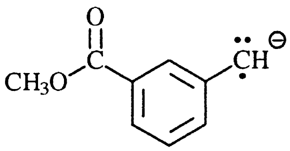
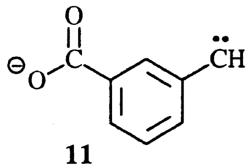
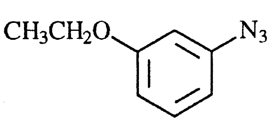
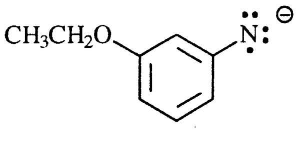
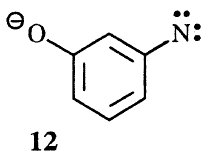
Scheme 1.

Table 1
Neutral precursors, carbanion intermediates and products of F_2 reactions (TMS = $SiMe_3$)

Entry	Precursor	Carbanion	Product
1.			**1** 
2.			**2** 
3.			**3** 
4.			**4** 
5.			**5** 
6.			**5** 
7.			**6** 
8.			**7** 
9.			**5** 

(*continued*)

Table 1 (*continued*)

Entry	Precursor	Carbanion	Product
10.		 	**8** 
11.		 	**9** 
12.			 **10**
13.			 **11**
14.			 **12**

only about 12 kcal/mol [28]. Thus, electron transfer is sufficiently exothermic to promote dissociation of the nascent $F_2^{\bullet -}$ ion (*vide infra*). The resulting fluoride ion then displaces the TMM radical anion by nucleophilic attack on the trimethylsilyl group. An analogous mechanism has been described for the formation of benzyne anions (e.g. **2**) from *bis*-trimethylsilylbenzenes (entry 2) [18].

The proposed mechanism for the anion-F_2 reaction is supported by several lines of evidence. First, when the electron binding energy of the TMS-substituted anion reactant exceeds EA(F_2), radical anion formation does not occur. For example, α-trimethylsilyacetate, $TMSCH_2CO_2^-$, and other TMS-containing carboxylates are unreactive with F_2 since the electron binding energies of carboxylate ions are $\geq$71 kcal/

mol [27]. For carbanions, electron transfer within the initial ion/molecule collision complex forming $F_2^{\cdot -}$ and a carbon radical should be thermodynamically favorable in most all cases because the electron binding energies of carbanions are typically much less than 71 kcal/mol [27]. If F^- (and not $F_2^{\cdot -}$) is the obligatory nucleophile in the final substitution step, then $F_2^{\cdot -}$ must dissociate within the intermediate complex. Dissociative electron transfer forming $F^- +$ F can occur if the electron affinity of the resulting carbon radical is less than $EA(F_2) - D_O$ [F-F$^-$] (ignoring the small ion induced-dipole attraction energy in the initial F_2/carbanion complex). The bond dissociation energy of $F_2^{\cdot -}$ has been measured to be 27.9 ± 1.6 kcal/mol [29]. Therefore, dissociative electron transfer is thermodynamically favorable when the electron binding energy of the TMS-substituted anion is less than $71 - 28 = 43$ kcal/mol.

Experimental evidence shows that the electron binding energy of the reactant carbanion does exert an influence on the efficiency of radical anion formation. Formation of TMM radical anion **1** from (2-trimethylsilylmethyl)allyl anion (entry 1) and oxyallyl radical anion **4** from (2-trimethylsiloxy)allyl anion (entry 4) occurs with much greater efficiency (product yield) than formation of acetate radical anion **5** from trimethylsilylacetate enolate (entry 5).* All three reactions are estimated to be exothermic by more than 20 kcal/mol. However, the first two reactants are allylic carbanions with estimated electron binding energies of ~12 kcal/mol, whereas the enolate ion precursor for **5** has an electron binding energy of about 42 kcal/mol [27]—close to the estimated cutoff value for dissociative electron transfer. This implies (but does not necessarily require) that $F_2^{\cdot -}$ dissociation plays a role in the mechanism of radical anion formation and, therefore, that F^- is the active nucleophile. Experiments comparing the reactivities of F^- and $F_2^{\cdot -}$ toward trimethylsilyl compounds are in progress.

If the radical anion produced in the final nucleophilic displacement step is a relatively strong base and, hence, a poor leaving group, then radical anion formation is inefficient or it fails entirely. For example, reaction between F_2 and $TMSCH_2^-$ [formed by reacting F^- with $CH_2(TMS)_2$] fails to produce the strongly basic methylene radical anion $CH_2^{\cdot -}$ [$\Delta H_{acid}(CH_3) = 409.1$ kcal/mol [27]], even though the overall reaction is exothermic. The influence of leaving group ability is also evident in the synthesis of α,3-dehydrotoluene anion **3** [30]. Reaction of F^- with trimethylsilylbenzene produces an adduct with a pentacoordinate silicon, $PhSiMe_3F^-$, as the major product, along with lesser amounts of phenyl anion. Thus, phenyl anion is a poor leaving group in the fluoride-induced desilylation reaction, which can be understood in terms of its strong basicity [$\Delta H_{acid}(C_6H_6) = 401.7$ kcal/mol [31]]. Similarly, reaction between 3-trimethylsilylbenzyl anion (entry 3) and F_2 produces, in addition to **3**, a significant yield of a product ion with the formula $C_{10}H_{15}FSi$, for which we propose the F^- adduct structure with a pentacoordinate silicon shown in Scheme 2. Collision-induced dissociation of this ion occurs by loss of $SiMe_3F$ to form **3** with a low energy requirement, consistent with the proposed structure. We consider this ion to be the "trapped" form of the intermediate in the final desilylation step, where the relative inefficiency of the displacement of a phenyl anion noted above allows the intermediate to become thermally stabilized as the F^- adduct by collisions with the helium bath gas.

As a practical matter we note that in many of F_2 reactions with silylated and nonsilylated carbanions, formation of the distonic radical anion is accompanied by intense signals due to the corresponding even-electron species one mass unit higher. For instance, the reactions of F_2 with the anion precursors for **1**, **2**, and **5** also produces 2-methylallyl anion, phenyl anion, and acetate anion, respectively. The origin of these side products has been identified as the unavoidable HF impurity in the helium/F_2 mixture [18]. The mechanism illustrated for 2-methylallyl anion formation in Scheme 3 involves protonation of the carbanion by HF, followed by reaction of the resulting F^- ion in the complex by attack on the TMS group. Analogous mechanisms can be envisioned for the other silylated carbanions listed in Table 1. For the

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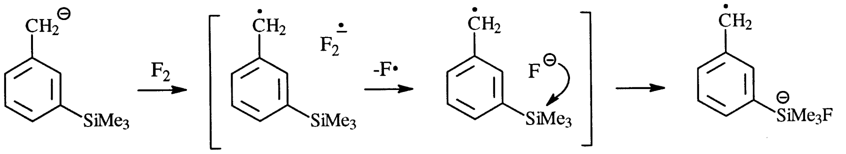
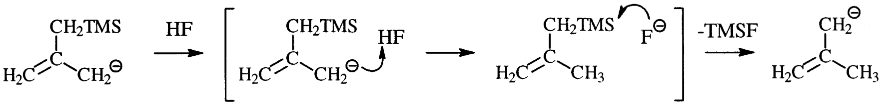
* Rate coefficients for reactions involving F_2 cannot be measured reliably due to the unavoidable presence of HF impurity in the helium-F_2 mixture.



Scheme 2.



Scheme 3.

nonsilylated species, the F^- intermediate apparently reacts by proton transfer, substitution, or elimination to yield the observed side products.

3.2. Variations

The radical anion synthesis procedure is flexible with respect to the types of neutral precursors that may be used, and the types of reactions taking place in the intermediate F^-/radical complex. *Bis*-TMS precursors are unnecessary in cases where the TMS-substituted carbanion can be formed selectively by proton abstraction. For example, deprotonation of trimethylsilylacetate by OH^- yields exclusively the enolate ion (entry 5); subsequent reaction with F_2 produces acetate radical anion **5**. Similarly, the benzylic carbanion precursor to **3** (entry 3) can be made by deprotonating 3-trimethylsilyltoluene with OH^-. However, in this case the *bis*-TMS precursor is preferred since the major product of the OH^- reaction with 3-trimethylsilyltoluene is Me_3SiO^- (m/z 89), and its ^{29}Si isotope peak is isobaric with **3**.*

We have found that the F^- ion produced by dissociative electron transfer can react with the transient radical within the intermediate ion/molecule complex by processes other than fluoride-induced desilylation. For example, an efficient method of forming acetate radical anion **5** (entry 6) is the reaction between F_2 and the enolate of acetic acid (formed by fluoride-induced desilylation of α-trimethylsilylacetic acid [32]), wherein the F^- ion deprotonates the nascent $\cdot CH_2CO_2H$ radical [20] (Scheme 4). Formation of the distonic allyl radical anion **6** illustrates this same principle with a neutral precursor bearing no TMS groups. Deprotonation of 6,6-dimethylfulvene with F^- occurs exclusively at one of the methyl groups [33] to yield isopropenylcyclopentadienyl anion. The intermediate F^- ion produced by dissociative electron transfer to F_2 then deprotonates the other methyl group in the radical to yield distonic ion **6**.

When the appropriate functional groups are present, the transient F^- ion can react with the intermediate radical by nucleophilic substitution and elimination reactions. For instance, deprotonated anisole [34] reacts with F_2 to yield (presumably *ortho*) dehydrophenoxide ion **7** (entry 8). In this case, F^- displaces the radical anion by an S_N2 reaction at the methyl group (Scheme 5). Similarly, ethylacetate enolate reacts with F_2 to produce acetate radical anion **5** (entry 9) by an F^--induced ethylene elimination in the final step (Scheme 6). These mechanisms illustrate the longevity of the intermediate ion/molecule complexes involved in the F_2 reactions, and are reminis-

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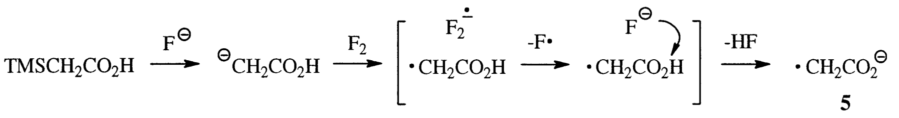
* Ambiguity regarding the site of initial desilylation may arise with *bis*-TMS precursors having non-equivalent TMS groups. For the *bis*-trimethylsilyltoluene indicated in entry 3, the benzylic TMS group is much more reactive towards F^- than the TMS group on the ring, so only the benzylic carbanion is produced [30]. Nevertheless, the order of desilylation may be irrelevant to the overall synthesis, because the negative charge and odd-spin may be delocalized in the radical anion.



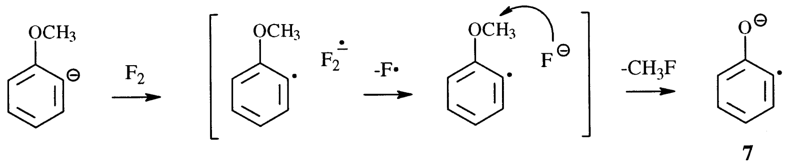
Scheme 4.

cent of the mechanisms proposed by Ingemann et al. for the formation of substituted-phenoxides from reactions of MeO^- with alkyl pentafluorophenyl ethers [35].

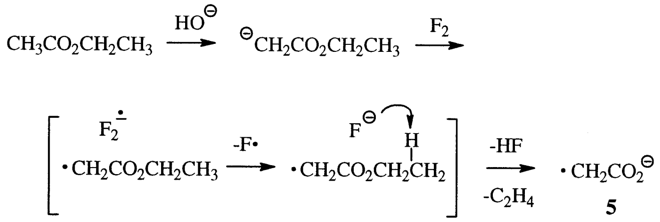
Distonic *biradical* anions (ionized triradicals) can be formed from precursors containing three TMS groups [21]. These species are required for measurements of doublet-quartet splittings in the corresponding triradicals by NIPES, and they represent a novel class of carbanions that may possess *triplet* ground states [36]. Fluoride-induced desilylation of 1,3,5-*tris*(trimethylsilyl)benzene followed by reaction of the resulting phenyl anion with F_2 yields the monosilylated *meta*-benzyne radical anion and the fully-desilylated $C_6H_3^-$ ion **8** (entry 10). Similarly, sequential reactions of F^- and F_2 with 1,3,5-*tris*(trimethylsilylmethyl)benzene produce *tris*-dehydromesitylene anion **9** (entry 11). The structures and reactivity of these ions have been investigated; **8** behaves like a singlet biradical, whereas **9** shows reactivity consistent with a triplet state [21]. An isomer of **8** was generated by Gronert and DePuy by CID of deprotonated fluorobenzene. This species was identified by its reactivity to be 2,3-dehydrophenyl anion [37]. $C_6H_3^-$ ions are also produced as secondary reaction products in the syntheses of *meta*- and *para*-benzyne anions by the F_2 approach [18]. For example, *m*-benzyne anion reacts with F_2 by dissociative electron transfer followed by proton transfer to F^- in the complex from the acidic 2-position of *m*-benzyne (ΔH_{acid} = 366 kcal/mol [38]) to yield 2,3-dehydrophenyl anion (Scheme 7). The $C_6H_3^-$ ion observed in the *p*-benzyne anion synthesis (entry 2) is believed to be the 3,4-dehydrophenyl anion isomer, although a ring-opened form has not been ruled out [21]. Analogous F_2-induced "dehydrogenations" of other carbanions have been observed. For instance, reaction of F_2 with allenyl anion (CH_2CCH^-) yields $C_3H_2^{\cdot -}$, C_3H^-, and $C_3^{\cdot -}$ with relative yields that are sensitive functions of the F_2 concentration.

By combining the propensity of $O^{\cdot -}$ for $H_2^{\cdot +}$ abstraction with the F_2 chemistry described above, we have been able to generate a novel class of anion containing a neutral carbene moiety and a relatively unreactive charge site, i.e. distonic *carbene* anions [22]. 3-Methoxytoluene reacts with $O^{\cdot -}$ to produce 3-methoxyphenylcarbene radical anion as the major $H_2^{\cdot +}$ abstraction product (entry 12). This ion reacts with F_2 by a sequential electron transfer—nucleophilic substitution mechanism analogous to Scheme 5 to produce 3-oxyphenylcarbene anion **10**. The structure of this ion has been identified by a derivatization approach, and its basicity has been determined by the kinetic method [22]. Scheme 8 illustrates the analogous synthesis of the phenylcarbene carboxylate ion **11** from methyl-*m*-toluate (entry 13).

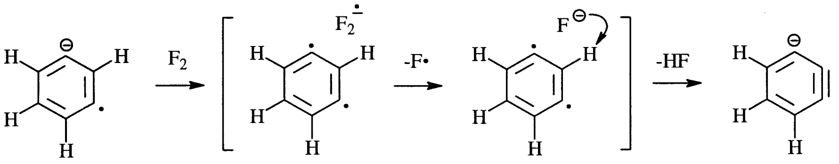
Finally, in the most recent extension of the F_2 chemistry, we have generated distonic *nitrene* anions from substituted phenylnitrene radical anions [39]. Dissociative electron ionization of phenylazide, PhN_3, produces phenylnitrene radical anion, $PhN^{\cdot -}$ [40]. Alkoxy derivatives such as 3-ethoxyphenylazide



Scheme 5.



Scheme 6.

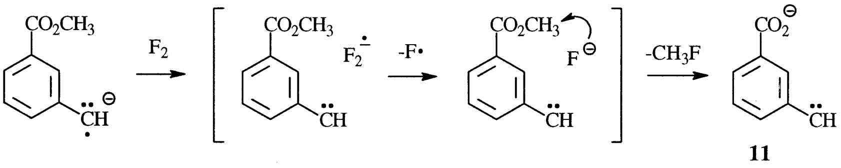


Scheme 7.

shown in entry 14 also produce nitrene anions upon electron impact. With high electron emission currents at the EI source of the flowing afterglow (~50 mA), N_2 loss from alkoxyphenylazides is accompanied by C–O bond cleavage to produce distonic nitrene anion **12**. However, a cleaner and higher-yield method of forming **12** is to react the 3-ethoxyphenylnitrene anion with F_2. In this reaction, formation of F^- by dissociative electron transfer from the nitrene anion (EA ≈35 kcal/mol [41]) is followed by an E2 elimination of ethylene from the ethoxy group. The properties and reactivity of this species are currently under investigation.

4. Conclusions

The gas-phase negative ion chemistry of molecular fluorine is versatile and mechanistically rich. The strong oxidizing power of F_2, the relatively low dissociation energy of $F_2^{\cdot -}$, and the high nucleophilicity and base strength of F^- all combine to make F_2 highly reactive towards organic anions, and capable of forming unusual products via multistep reactions within long-lived ion/molecule complexes. We have investigated some aspects of this chemistry with the aim of developing practical synthetic procedures for distonic radical anions and other theoretically-interesting negative ions. We have shown how TMS-substituted carbanions and negative ions containing acidic or substitutionally labile functional groups can react with F_2 in a predictable manner to produce novel product ions containing a neutral radical, biradical, carbene, or nitrene moiety. Evolving interests in the properties, reactivity, and spectroscopy of these species will no doubt motivate further developments in the gas-phase synthesis of distonic ions using molecular fluorine.



Scheme 8.

Acknowledgements

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