Generation of Specific Isomeric Carbanions in the Gas Phase

Sir:

The study of the reactions of organic anions in the gas phase is a subject of increasing interest, since it provides information about the intrinsic reactivity¹ and basicity of ions,² the electron affinity of radicals,³ and other fundamental properties of ions unencumbered by solvation. ⁴ Moreover, negative ion chemical ionization mass spectrometry is becoming a tool of increasing importance for chemical analysis and structural elucidation.⁵ A common method for the production of such anions is proton abstraction from neutral molecules using the strong gas phase bases, hydroxide or alkoxide ions.

However, carbanion production by proton abstraction is often ambiguous and unsatisfactory. There may be several abstractable protons in the hydrocarbon molecule, so that mixtures of anions may be formed. In some cases, as in proton abstraction from 2-pentene, the relative acidity of the two types of allylic protons is similar, and formation of both anions is expected. However, even in molecules where the proton acidities are expected to differ substantially, as in propyne, we have found in our flowing afterglow system⁶ that a majority of the less stable anion is formed:

$$OH^- + CH_3C \equiv CD \xrightarrow{<40\%} CH_3C \equiv C^- + HOD \quad (1)$$

$$OH^- + CH_3C \equiv CD \xrightarrow{> 60\%} - CH_2C \equiv CD + H_2O \quad (2)$$

A more subtle and hence more dangerous complication is the observed base promoted rearrangement of certain molecules in the very ion-molecule complex in which proton abstraction occurs.⁷ Thus double-bond migration and cis-trans isomerization may occur, leading to anions of unknown or unexpected structure.

We report herein that many organic anions can be generated efficiently and unambiguously by reaction of their trimethylsilyl derivatives with fluoride ion (easily formed by electron impact on NF_3 or CF_4). For example, each of the two isomeric $C_3H_3^-$ ions can be separately generated in this manner:

$$F^{-} + CH_{3}C \equiv CSi(CH_{3})_{3}$$

$$\rightarrow CH_{3}C \equiv C^{-} + FSi(CH_{3})_{3} \quad (3)$$

$$F^{-} + HC \equiv CCH_2Si(CH_3)_3 \rightarrow HC \equiv CCH_2^{-} + FSi(CH_3)_3$$
(4)

The success of this method must depend upon the great strength of the silicon-fluorine bond which compensates for the greater electron affinity of fluorine atoms relative to organic radicals. The two ionic products of eq 3 and 4 differ substantially in their reactivity, confirming their isomeric structures. For example, the propargyl anion reacts with molecular oxygen seven times more rapidly than does the methyl acetylide anion⁸ and large differences in rates or products are observed with D₂O and other reagents.

In addition to anions stabilized by triple bonds, the fluoride-silane displacement reactions are useful for producing a variety of allyl and benzyl anions. Trimethylsilyl derivatives are generally easily prepared⁹ and can be handled without difficulty. We have applied this method to generate anions from the trimethylsilyl derivatives of propylene, cis- and trans-2-butene and toluene. We have not yet been successful in creating less stable anions; tetramethylsilane and vinyl and cyclopropyl trimethylsilane form adducts with F⁻ and only traces of $C_6H_5^-$ are produced from phenyl trimethylsilane.

An equally important advantage of this method is production of anions in the absence of their hydrocarbon precursors. These acidic precursors frequently react with product ions to regenerate the initial carbanion and thus greatly complicate the determination of rate constants and product distributions.

In conclusion, the displacement reaction of fluoride ion with trimethylsilyl derivatives allows the specific production of a single isomeric species in the absence of other anions or acidic neutrals; this method, therefore, will greatly facilitate the detailed correlation of structure and reactivity of gas phase organic anions.

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C. H. DePuy,* Veronica M. Bierbaum,* L. A. Flippin Joseph J. Grabowski, Gary K. King, Robert J. Schmitt

Department of Chemistry, University of Colorado Boulder, Colorado 80309 Received May 23, 1979

Gas-Phase Reactions of Carbanions with Triplet and Singlet Molecular Oxygen

Sir:

We report herein the ion-molecule reactions of molecular oxygen, in both its ground state $(X^{3}\Sigma_{g}^{-})$ and first electronically excited state $(a^{1}\Delta_{g})$,¹ with organic anions in the gas phase. Molecular oxygen promises to be a powerful reagent for gas-phase chemical degradation and structural elucidation of ions since it appears to induce specific cleavage reactions which reflect the various sites of negative charge in the anion.

We generate organic anions in our flowing afterglow system² by proton abstraction with amide from neutral organic precursors or by the reaction of F^- with silanes.³ The ions are collisionally relaxed before they are mixed with the reactant molecular oxygen. The reactant and product ionic species are monitored by mass spectrometric detection.

As a typical example of a delocalized species, the 2,4-hexadienyl anion reacts readily with ground-state oxygen by addition and cleavage at each nonterminal carbon atom which bears a negative charge, to generate enolate anions of m/e 43, 57, and 69 (eq 1).

$$CH_{3}-CH^{\pm}CH^{\pm}CH^{\pm}CH^{\pm}CH^{\pm}CH_{2} + {}^{3}O_{2} \rightarrow CH_{3}-CH=CH-CHO + O-CH=CH_{2} (1a)$$

$$\rightarrow$$
 CH₃-CH=CH-O + OHC-CH=CH₂ (1b)
m/e 57

$$\rightarrow$$
 CH₃CHO + O-CH=CH-CH=CH₂ (1c)
m/e 69

$$\leftrightarrow$$
 CH₃-CH=CH-CH=CH-O + CH₂O (1d)
m/e 83

The anion⁴ (CH₂==CHCH₂CH····CH₂)⁻ of 1,5hexadiene exhibits a simpler product ion spectrum upon reaction with ${}^{3}O_{2}$. Hydride transfer to form HO₂⁻ and the hexatriene neutral is the dominant mechanism⁵ and cleavage processes produce only mass 43 (CH₂CHO⁻). The absence of masses 57 and 69 reflects the absence of the appropriate charge distribution in the reactant ion. These two isomeric hexadienyl anions are therefore distinguishable by their chemical ionization spectrum with ${}^{3}O_{2}$. This application of molecular oxygen as a reagent gas is especially useful since the isotope exchange reactions with CH₃OD do not distinguish these isomers, each species incorporating seven deuterium atoms.⁵

Reactions of alkenyl anions 6 with oxygen exhibit several reaction pathways (eq 2) as evidenced by the 1-pentenyl

$$CH_2=CH-\bar{C}H-CH_2-CH_3 + {}^{3}O_2 + O_2^- + CH_2=CH-CH-CH_2-CH_3$$
(2a)
+ HO_2^- + CH_2=CH-CH=CH-CH_3 (2b)

$$\rightarrow CH_2 = CH - CH = CH - CH_2 + H_2O_2 \quad (2c)$$

$$\rightarrow CH_2 = CHO^- + OHC - CH_2 - CH_3^- (2d)$$

$$\rightarrow OH^{-} + OHC - CH = CH - CH_{2} - CH_{3}$$
 (2e)

species. Simple charge transfer indicates that the electron affinity of molecular oxygen exceeds that of the hydrocarbon radical. Pathway 2c is intriguing and presumably arises from a second ion-molecule reaction within the long-lived complex which also produces HO_2^- and pentadiene.

The anions of toluene and of m and p-xylene react slowly with ${}^{3}O_{2}$ to generate OH⁻ as 99% of the product ion spectrum. In contrast, the *o*-xylene anion exhibits three major reaction pathways (eq 3). Formation of the anion of methyl benzaldehyde (eq 3b) is presumably enhanced in the intermediate

$$\rightarrow \bigcirc^{CH_3}$$
 + OH^{- (3c)}

$$\bigcirc \overset{\mathsf{CH}_3}{\bigcirc} \overset{\mathsf{CH}_2}{\overset{\mathsf{CH}_2}{\longrightarrow}} + \overset{\mathsf{3O}_2}{\overset{\mathsf{O}}{\longrightarrow}} \overset{\mathsf{CH}_2}{\overset{\mathsf{CHO}}{\longrightarrow}} + \overset{\mathsf{H}_2}{\overset{\mathsf{O}}{\bigcirc}} \overset{(3\mathsf{D})}{\overset{\mathsf{O}}{\longrightarrow}}$$

$$\rightarrow$$
 \bigcirc $^{CH_3}_{I}$ + $CH_2O^{(3c)}$

complex by the proximity of the methyl group to OH^- formation. Equation 3c is the aromatic analogue of the previously described cleavages. *o*-Xylene can therefore be distinguished from the meta and para isomers with molecular oxygen as reagent, whereas isotope exchange reactions do not distinguish these species.⁷

Many anions are completely unreactive toward oxygen even though analogous exothermic channels exist, for example, eq 4 and 5. In an attempt to surmount the apparent energy barrier for these processes, we generated the first electronically excited state of molecular oxygen, $O_2(a^1\Delta_g)$, by incorporating a mi-

$$CH_3^{\circ} + {}^3O_2 \xrightarrow{+} HO_2^{\circ} + CH_2^{\circ}$$
 (4)
 $\Delta H \simeq -20 \text{ kcal/mole}$

$$\overline{CH}_2 NO_2 + {}^{3}O_2 \not \rightarrow NO_3 + CH_2 O$$

$$\Delta H \simeq -75 \text{ kcal/mole}$$
(5)

crowave discharge on the oxygen inlet of the flowing afterglow. In this manner, up to 10% of the total O₂ flow⁸ can be converted into singlet oxygen, which lies 22 kcal/mol above the ground state, with a radiative lifetime of ~45 min.⁸

The anion of nitromethane reacts readily with singlet oxygen to form three major products⁹ (eq 6). The first two pathways

$$\bar{C}H_2NO_2 + {}^1O_2 \rightarrow NO_3 + CH_2O$$
 (6a)

$$\rightarrow OH^- + OHCNO_2$$
 (6b)

$$+ NO_2 + H_2O + CO$$
 (6c)

represent a direct analogy to the mechanisms observed for other ions with ground-state oxygen. The third product probably arises from further reaction of OH^- with $OHCNO_2$ within a long-lived complex. The anion of acetonitrile behaves in a similar manner.

Methoxide reacts by hydride transfer to singlet oxygen (eq 7). Subsequent oxidation of formaldehyde by HO_2^- before

$$CH_{3}O^{-} + {}^{1}O_{2} \rightarrow HO_{2}^{-} + CH_{2}O$$
(7a)
$$\rightarrow HCO_{2}^{-} + H_{2}O$$
(7b)

separation of these products forms the formate ion and water. Similarly the reaction of ethoxide proceeds by hydride transfer (eq 8). However, owing to the acidity of the neutral product in eq 8a, proton abstraction by HO_2^- rather than oxidation

$$CH_{3}CH_{2}O^{-} + {}^{1}O_{2} \rightarrow HO_{2}^{-} + CH_{3}CHO$$
(8a)
$$\rightarrow CH_{2}CHO^{-} + H_{2}O_{2}$$
(8b)

generates the second pathway. The isopropoxide ion reacts in direct analogy to ethoxide; however, the *tert*-butoxide ion, lacking an α hydrogen for hydride transfer, is unreactive toward ${}^{1}O_{2}$. The hydroperoxide anion, generated in eq 7a and 8a reacts further with singlet molecular oxygen by oxidation and charge transfer (eq 9).

$$HO_2^{-} + {}^{1}O_2^{-} + O_3^{-} + OH$$
 (9a)

$$\rightarrow O_2 + HO_2$$
 (9b)

The nature of the energy barrier in these carbanion-oxygen reactions is an intriguing mechanistic question. Interaction of an anion with ${}^{3}O_{2}$ requires a change in multiplicity;¹⁰ we suggest that this occurs after electron transfer from the anion to O_{2}^{11} since a change of electron spin occurs readily in O_{2}^{-} (eq 10). Carbanions of radicals with electron affinities ≤ 20

$$R^{-} + O_2 \rightarrow [R^{*} + O_2^{-}] \rightarrow \text{products}$$
 (10)

kcal react with ground-state oxygen while those of higher electron affinities do not, presumably because reaction 10 has become unfavorable. Use of ${}^{1}O_{2}$, whose reaction with an anion does not require a spin change (or for which electron transfer is 22 kcal/mol more favorable), then allows the reactions to proceed for these more stable anions.

In conclusion, molecular oxygen, in both its ground state and first electronically excited state, reacts with carbanions to form cleavage products which are diagnostic of the reactant ion structure. Oxygen therefore serves as a powerful tool for the chemical degradation and structural analysis of gas-phase carbanions.

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Robert J. Schmitt, Veronica M. Bierbaum,* C. H. DePuv* Department of Chemistry, University of Colorado Boulder, Colorado 80309 Received May 23, 1979

Photoreaction of Valence-Bond Isomers of Hexakis(trifluoromethyl)oxepin. Synthesis of a Stable Oxetene Derivative

Sir:

The photoreaction of perfluoroalkylated compounds is especially interesting because of the possible isolation of strained compounds by the "perfluoroalkyl effect".¹ Previously we reported the reduction of hexakis(trifluoromethyl)benzvalene ozonide with triphenylphosphine, affording two valence-bond isomers of hexakis(trifluoromethyl)oxepin,² hexakis(trifluoromethyl)-2-oxabicyclo[3.2.0]hepta-3,6-diene (1) and hexakis(trifluoromethyl)-3-oxatricyclo[4.1.0.0^{2,7}]heptene (2) (Scheme I).

We now report the photoreaction of 1 and 2 including formation of a new stable oxetene derivative. Irradiation³ of a perfluoropentane solution of 1 in a silica tube at room temperature gave no isomeric product. Irradiation of 2 under the same condition gave a mixture of Z and E forms (3 and 4) of 1,2,3-tris(trifluoromethyl)-3-[1,2,3-tris(trifluoromethyl)cyclopropenyl]propenone in a quantitative yield (Scheme II). These isomers (3 and 4) could not be separated even by VPC. The molar ratio of 3 and 4 was 1:1. The structural assignment of 3 and 4 was based on the results of the following reactions and on their spectral data. When a mixture of 3 and 4 in pentane was heated at 140 °C and the reaction was followed by 19 F NMR spectra, only the Z isomer 3 regenerated 2 and the E isomer 4 remained unchanged. On the other hand, irradiation of a mixture of 3 and 4 in perfluoropentane filtered with Pyrex gave only one product (5) in a quantitative yield. The ¹⁹F NMR spectrum⁴ of **5** in a pentane solution showed five multiplets centered at -3.5, -2.9, 1.4, 7.4, and 11.8 ppm (the intensity ratio of signals was 2:1:1:1:1⁵).

The IR spectrum of 5 in pentane revealed absorption bands at 1900 and 1735 cm⁻¹, ascribable to the cyclopropene double bond⁶ and the oxetene ring double bond,⁷ respectively, and the mass spectrum of 5 showed m/e 502 (M⁺) (calcd for C₁₂F₁₈O, mol wt 502). The UV spectrum of 5 showed only one absorption maximum at 207 nm ($\epsilon 2.80 \times 10^3$, in *n*-hexane), while that of the mixture of 3 and 4 showed three absorptions at 198



Scheme II

1 <u>hr</u> -> No Reaction



 $(\epsilon 3.72 \times 10^3)$, 250 (sh, 146), and 305 nm (31). These data show that 5 has no carbonyl group, while 3 and 4 have.

From these data we concluded that 5 is a perfluoromethylated cyclopropenyloxetene,⁸ which is a colorless and stable liquid at room temperature and is exclusively converted into the *E* isomer 4 of the enone on being heated at 80 °C (T = 5.7h in pentane). This result of thermal reaction of 5 is consistent with the results of the thermal reaction of transiently formed oxetene derivatives, which has been reported previously.⁹ From the thermal reaction of 5, pure E isomer 4 was isolated in a quantitative yield: colorless liquid; ¹⁹F NMR (pentane) - 3.6, -2.1, 3.2 (group i), 12.4 ppm (COCF₃) (each signal is broad,

intensity ratio 3:1:1:1); IR spectrum (pentane) ν (C==O) 1890 (cyclopropene double bond), 1770 cm⁻¹; mass spectrum m/e502 (M⁺) (calcd for $C_{12}F_{18}O$, mol wt 502). The ¹⁹F NMR of Z isomer 3 is deduced from those of the mixture of 3 and 4: -7.4, -4.2, 3.2 (group i), 13.3 ppm (COCF₃) (relative ratio 1:3:1:1).

A very rapid equilibrium between 3 and 4 was observed on the irradiation of the isolated isomer (4). This result shows that 3 and 4 are Z/E isomers. Moreover, regeneration of 2 from 3 (Z form) and not from 4 (E form) by thermal reaction supports each of the assigned structures, since regeneration of 2 from **3** is considered to be a thermally allowed $(\pi 2_s + \pi 2_s + \pi 2_s)$ concerted process and, in the case of 4 (E form), the thermally allowed concerted process cannot regenerate 2 because of the trans double bond.

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