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Reactions of Carbanions with Triplet and Singlet Molecular Oxygen

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The gas phase reactions of carbanions with molecular oxygen in both its ground state ($X^3\Sigma_g^-$) and first electronically excited state ($a^1\Delta_g$) have been studied by the flowing afterglow technique. Reactions include cleavage processes, charge transfer, hydride transfer, formation of hydroxide ion and processes which involve secondary reactions within a long-lived complex. The mechanisms of the reactions are discussed. The usefulness of molecular oxygen as a reagent for the structural degradation and analysis of gas phase organic anions, including isomeric species, is described.

Introduction

In our flowing afterglow studies of the gas phase chemistry of organic ions, we have two distinct but strongly interrelated goals. The first is to explore the "intrinsic" chemistry of organic ions, that is, chemistry in the absence of solvent molecules and hence in the absence of solvation. We are interested in determining rate constants for ion-molecule reactions, products and their distribution, mechanisms of reactions, energy disposal, and thermochemical quantities. Our second goal, which is more relevant to the subject of the conference on negative chemical ionization mass spectrometry, is to develop methods for the structural analysis of organic ions. We are interested in developing ion-molecule reactions with a view to their use in negative chemical ionization mass spectrometry. We study primarily simple prototype molecules and attempt to fill one of the major needs discussed at this conference: an understanding of the basic chemistry and reaction mechanisms involved. This is essential to the proper use and advancement of NCIMS as an invaluable analytical tool.

In this paper we will first briefly describe the flowing afterglow technique and then discuss some reactions of organic negative ions with molecular oxygen. Oxygen can be a powerful reagent, since it appears to induce specific cleavage reactions which reflect the various sites of negative charge in the ion (*1*).

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Experimental

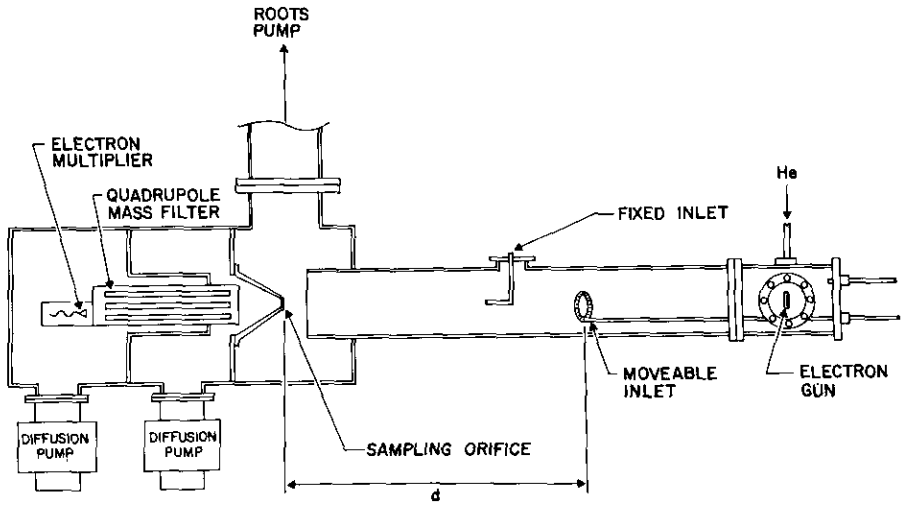
The flowing afterglow apparatus (*2*) is shown in Figure 1. The heart of the system is a flow tube (1 m long, 8 cm diameter) in which ions are generated and their reactions with molecules occur. Downstream there is a differentially pumped system for the analysis and detection of the ions. A typical experiment, for example, the reaction of the allyl anion with oxygen is performed in the following manner. A large calibrated flow of purified helium is pumped through the flow tube to establish a pressure of about 0.5 torr and flow velocities of about 100 m/sec. To generate primary ions, we introduce small flows of other gases past the electron impact ionizer, for example,

$$N_2O + e^- \rightarrow O^- + N_2 \quad (1)$$

$$O^- + CH_4 \rightarrow OH^- + CH_3 \quad (2)$$

$$NH_3 + e^- \rightarrow NH_2^- + H \quad (3)$$

Both amide and hydroxide are relatively strong bases which will abstract protons from most organic compounds. Therefore addition of propyl-



ene downstream of the ion source generates the allyl anion:

$$NH_2^- + C_3H_6 \rightarrow C_3H_5^- + NH_3 \quad (4)$$

This plasma then flows about 20 cm to allow the ions to undergo thousands of collisions with helium and thereby lose any excess energy; in this region the flow profile also becomes nonturbulent and well-defined. Finally, through the moveable inlet molecular oxygen is added and the allyl anion-oxygen reaction proceeds from this point to the point of sampling of the plasma. The reaction distance and therefore the reaction time can be varied by changing the position of the moveable inlet. Most of the reaction mixture is pumped away but a small fraction is sampled through an orifice, analyzed by a quadrupole mass filter, and detected with an electron multiplier. The total ion spectrum is monitored as a function of reaction time, pressures and flow rates.

We use the flowing afterglow technique to study gas phase ion-molecule reactions because it offers a variety of advantages: (1) the ionic and neutral reactants are at thermal energy; (2) ion production is versatile; (3) due to the flow nature of the technique, relatively unstable neutral reactants [e.g., $O_2(^1\Delta)$] can be generated and studied; (4) energy variability is straightforward; (5) kinetics are easily determined. In addition, the flowing afterglow technique is constantly undergoing developments which greatly enhance its capabilities.

Results and Discussion

The products of the reaction of the allyl anion with molecular oxygen are given in Eq. (5). [Bohme and Young have reported (*3*) the reactions of $C_3H_5^-$, $C_4H_7^-$, and $C_3H_3^-$ with molecular oxygen.]

$$CH_2{=}CH{-}CH_2^- + O_2 \xrightarrow{90\%} O_2^- + CH_2{=}CH{-}\dot{C}H_2 \quad (5a)$$

$$\xrightarrow{8\%} OH^- + CH_2{=}CH{-}CHO \quad (5b)$$

$$\xrightarrow{1\%} CH_2{=}CH{-}O^- + CH_2O \quad (5c)$$

Ninety percent of the reaction proceeds by simple charge transfer, indicating that the electron affinity of oxygen exceeds that of the allyl radical [Eq. (5a)]. The minor products of m/e 17(OH^-) and m/e 43(CH_2CHO^-) arise in the following manner: molecular oxygen adds at the site of negative charge; cleavage occurs across the O - O bond and either across the C—H bond [to generate hydroxide ion and the neutral aldehyde, Eq. (5b)] or across the C—C bond [to generate the enolate anion and formaldehyde, Eq. (5c)].

The reaction of oxygen with the pentadienyl anion, in which the charge resides on the central and terminal carbon atoms, produces hydroxide ion and two enolate ions:

$$\overset{\delta-}{CH_2}{\cdots}\overset{\delta-}{CH}{\cdots}CH{\cdots}CH{\cdots}\overset{\delta-}{CH_2} + O_2$$

$$\rightarrow CH_2{=}CH{-}O^- + OHC{-}CH{=}CH_2 \quad (6a)$$

$$OH^- + CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2 \quad (6b)$$

$$\rightarrow OH^- + CH_2{=}CH{-}CH{=}CH{-}CHO \quad (6c)$$

$$\rightarrow CH_2{=}CH{-}\dot{C}H{=}CHO^- + CH_2O \quad (6d)$$

Addition of molecular oxygen has occurred at all sites of negative charge in the anion followed by specific cleavages. This type of reaction therefore promises to be valuable for the specific structural degradation of organic anions.

New reaction channels become evident for the 1-pentenyl anion:

$$\overset{\delta-}{CH_2}\cdots CH\cdots\overset{\delta-}{CH}-CH_2-CH_3 + O_2$$

$$\rightarrow O_2^- + CH_2{=}CH-CH-CH_2-CH_3 \quad (7a)$$

$$\rightarrow HO_2^- + CH_2{=}CH-CH{=}CH-CH_3 \quad (7b)$$

$$\rightarrow CH_2{=}CH-CH{=}CH-CH_2^- + H_2O_2 \quad (7c)$$

$$\rightarrow CH_2{=}CHO^- + OHC-CH_2-CH_3 \quad (7d)$$

$$\rightarrow OH^- + OHC-CH{=}CH-CH_2-CH_3 \quad (7e)$$

$$\not\rightarrow {}^-O-CH{=}CH-CH_2-CH_3 + CH_2O \quad (7f)$$

Simple charge transfer [Eq. (7a)] is again evident. Now, however, hydride transfer from the carbanion to oxygen [Eq. (7b)] is a major product; this process may be enhanced by the stability of the conjugated diene that is formed. Reaction (7c) is intriguing and presumably arises from a long-lived complex in which HO_2^- and pentadiene were formed; before the species separate, the basic hydroperoxide anion encounters the acidic protons in pentadiene and a second ion-molecule reaction occurs within the same single encounter. The neutral pentadiene formed in Eq. (7b) could not separate from HO_2^- and then undergo later ionization since its density is comparable to ion densities; the pentadiene molecules are lost in a sea of other neutrals and essentially never encounter another ion. We have numerous examples of secondary reaction processes of this type which occur within a single ion-molecule collision complex (*4*). The reactions given in Eqs. (7d,e,f) result from oxygen addition/cleavage processes discussed above; the absence of pathway (7f) in this case parallels the small contribution of reaction (5c) for the allyl anion.

Hydride transfer to form HO_2^- can become the dominant pathway. For example, the methyl butenyl anion reacts with oxygen to yield 99% HO_2^- [Eq. (8)], while cyclohexadienyl anion (*5*) reacts with about 95% efficiency to yield HO_2^- [Eq. (9)].

$$CH_3-CH{=}C(CH_3)CH_2^- + O_2$$

$$\xrightarrow{99\%} HO_2^- + CH_2{=}CH-C(CH_3){=}CH_2 \quad (8)$$

$$C_6H_7^- + O_2 \xrightarrow{95\%} HO_2^- + C_6H_6 \quad (9)$$

This monopoly on a single reaction channel obscures some structural data but does provide strong evidence for the formation of a conjugated diene or an aromatic molecule. Moreover it provides a convenient source of HO_2^- which has proven to be an excellent gas phase oxidizing agent.

The reaction with molecular oxygen allows one to distinguish among isomeric carbanions. For example, the anion formed by proton abstraction from 2,4-hexadiene reacts with molecular oxygen to form predominantly three enolate ions [Eqs. (10)].

$$CH_3-\overset{\delta-}{CH}\cdots CH\cdots\overset{\delta-}{CH}\cdots CH\cdots\overset{\delta-}{CH_2} + O_2$$

$$\rightarrow CH_3-CH{=}CH-CHO + {}^-O-\underset{m/e\ 43}{CH{=}CH_2} \quad (10a)$$

$$\rightarrow \underset{m/e\ 57}{CH_3-CH{=}CH}-O^- + OHC-CH{=}CH_2 \quad (10b)$$

$$\rightarrow CH_3CHO + -O-CH-\underset{m/e\ 69}{CH-CH}=CH_2 \quad (10c)$$

The hyproperoxide ion is also formed in small quantities. In contrast to these results, the isomeric anion formed from 1,5-hexadiene exhibits a simpler product ion spectrum:

$$CH_2=CH-CH_2-\overset{\delta-}{CH}\cdots CH\cdots\overset{\delta-}{CH_2} + O_2$$

$$\rightarrow CH_2{=}CH-CH{=}CH-CH{=}CH_2 + \underset{m/e\ 33}{HO_2^-} \quad (11a)$$

$$\rightarrow CH_2{=}CH-CH_2-CHO + {}^-O-\underset{m/e\ 43}{CH{=}CH_2} \quad (11b)$$

In the latter case, HO_2^- is the major product; masses 57 and 69 are absent, reflecting the absence of the appropriate charge distribution in the reactant ion. The ability of molecular oxygen to distinguish these isomers is interesting and useful since these anions can not be distinguished by hydrogen-deuterium exchange reactions. The reaction of either hexadienyl anion with CH_3OD produces seven exchanges (*4*); this is precisely be-

cause isomerization occurs during the exchange process.

The hexadienyl anions in Eqs. (10) and (11) were produced by proton abstraction from the parent neutrals with amide anion; this process preserves the isomeric integrity of the species. If, however, we use hydroxide ion as the precursor base, the spectra of the hexadienyl anions upon reaction with oxygen become similar. This occurs since hydroxide ion can cause isomerization in the same neutral encounter in which proton abstraction occurs (*4*).

The benzyl anion exhibits two reaction pathways with oxygen:

$$C_6H_5CH_2^- + O_2 \xrightarrow{98\%} OH^- + C_6H_5CHO \quad (12a)$$

$$\xrightarrow{1\%} C_6H_5O^- + CH_2O \quad (12b)$$

Charge transfer is endothermic and is not observed. Instead, most of the product corresponds to addition of oxygen at the site of negative charge and cleavage to produce hydroxide ion; only 1% of the product corresponds to cleavage into the ring with phenoxide formation.

The xylenes present an interesting example of the utility of molecular oxygen as a reagent. In analogy to the benzyl anion, the anions of *m*- and *p*-xylene react slowly with oxygen to yield OH^- as 99% of the product. In contrast, the *o*-xylene anion yields three products of comparable intensity:

$$o\text{-}CH_3C_6H_4CH_2^- + O_2 \rightarrow OH^- + o\text{-}CH_3C_6H_4CHO \quad (13a)$$

$$\rightarrow o\text{-}^-CH_2C_6H_4CHO + H_2O \quad (13b)$$

$$\rightarrow o\text{-}CH_3C_6H_4O^- + CH_2O \quad (13c)$$

The second pathway [Eq. (13b)] must occur as a secondary process within a long-lived complex and is presumably facilitated by the proximity of the OH^- to the methyl substituent. The anions of *o*-, *m*-, and *p*-xylenes are not distinguished by hydrogen-deuterium exchange reactions, since all three anions incorporate five deuterium atoms (*6*).

If the methyl group in the anion of xylene is replaced by the electron withdrawing aldehyde substituent, the resulting anion is unreactive toward oxygen:

$$p\text{-}^-CH_2C_6H_4CHO + O_2 \rightarrow \text{no reaction} \quad (14)$$

We have found a number of ions which do not react with molecular oxygen even though exothermic pathways exist. For example, the methoxide ion could react by hydride transfer to generate the hydroperoxide ion and formaldehyde in direct analogy with other observed reactions, while the anion of nitromethane could react to form nitrate ion and formaldehyde. Neither of these reactions occurs [Eqs. (15) and (16)].

$$CH_3O^- + O_2 \not\rightarrow HO_2^- + CH_2O \quad \Delta H \simeq -20 \text{ kcal/mole} \quad (15)$$

$$^-CH_2NO_2 + O_2 \not\rightarrow NO_3^- + CH_2O \quad \Delta H \simeq -75 \text{ kcal/mole} \quad (16)$$

The nonoccurrence of exothermic channels is usually explained in terms of an activation energy or energy barrier somewhere in the reaction process even though the overall process is exothermic. If we compare those anions that are reactive to oxygen with those anions that are not, we find that the first group have parent radicals with electron affinities of about 20 kcal/mole or less, while the second group have parent radicals with higher values of electron affinity. There appears to be an inverse correlation between electron affinity and reactivity toward oxygen. It is therefore possible that the initial step in the reaction of the carbanion involves electron transfer to molecular oxygen, followed by addition and cleavage. When this transfer becomes unfavorable due to the high electron affinity of the organic radical, the reaction no longer proceeds. This idea of initial electron transfer is consistent with two considerations: (1) charge transfer is observed as the net reaction whenever it is exothermic; (2) the proposition of charge transfer eliminates problems involving electron spin. Carbanions are generally spin singlets while molecular oxygen is a triplet in its ground state. Therefore, interaction between a carbanion and oxygen to form a bond must involve a change in multiplicity. If an electron is transferred to oxygen, it is known that a change of electron spin occurs readily in O_2^- and hence bond formation is enhanced.

The first electronically excited state of molecular oxygen is a spin singlet, $O_2(a^1\Delta_g)$ and lies 22 kcal/mole above the ground state triplet, $O_2(X^3\Sigma_g^-)$ (*7*). Use of $^1O_2$ in processes such as Eq. (15) and (16) may enhance the reactivity of carbanions due to the fact that a change of spin is no longer required or the electron affinity of $^1O_2$ is 22 kcal/mole greater than that of $^3O_2$.

We therefore incorporated a microwave discharge on the molecular oxygen inlet of our flowing afterglow apparatus. Under the conditions of our experiments, up to 10% $^1O_2$ can be produced, based on the measurements of other researchers (*7*).

The reaction of singlet oxygen with the anion of nitromethane proceeds readily to give three products [Eqs. (17)]

$$^-CH_2NO_2 + {}^1O_2 \rightarrow NO_3^- + CH_2O \quad (17a)$$

$$\rightarrow OH^- + OHCNO_2 \quad (17b)$$

$$\rightarrow NO_2^- + H_2O + CO \quad (17c)$$

The first two pathways occur in direct analogy to previously discussed mechanisms: addition at the negative charge with two possible directions of cleavage. The third product presumably occurs from secondary attack by OH^- on $OHCNO_2$ within a long-lived complex.

Since oxygen atoms and ozone molecules can also be formed in microwave discharges under some conditions, it is important to establish that these species are not the origin of the observed reactions. This is easily demonstrated with ion chemistry. The hydroxide ion reacts readily with both O (*8*) and O_3 (*9*), but is unreactive toward $^1O_2$.

$$OH^- + {}^1O_2 \rightarrow \text{No reaction} \quad (18)$$

$$OH^- + O \rightarrow HO_2 + e^- \quad k = 2 \times 10^{-10}\ cm^3/\text{molecule-sec} \quad (19)$$

$$OH^- + O_3 \rightarrow O_3^- + OH \quad k = 9 \times 10^{-10}\ cm^3/\text{molecule-sec} \quad (20)$$

Therefore the absence of reaction of OH^- with the microwave discharge operating demonstrates the absence of O and O_3.

The anion of acetonitrile reacts with $^1O_2$ to yield products similar to those in Eq. (17):

$$^-CH_2CN + {}^1O_2 \rightarrow OCN^- + CH_2O \quad (21a)$$

$$\rightarrow OH^- + OHCCN \quad (21b)$$

$$\rightarrow CN^- + H_2O + CO \quad (21c)$$

The alkoxide ions undergo an interesting series of reactions with $^1O_2$. The methoxide ion reacts by hydride transfer [Eq. (22a)], and subsequent oxidation of formaldehyde within a long-lived complex generates formate ion and water [Eq. (22b)].

$$CH_3O^- + {}^1O_2 \rightarrow HO_2^- + CH_2O \quad (22a)$$

$$\rightarrow HCO_2^- + H_2O \quad (22b)$$

Similar reactions occur for ethoxide ion and isopropoxide ion. However, the *tert*-butoxide ion, lacking an α hydrogen for hydride transfer, is unreactive toward $^1O_2$.

$$(CH_3)_3CO^- + {}^1O_2 \rightarrow \text{no reaction} \quad (23)$$

A final example of the usefulness of molecular oxygen as a probe of the structure of ions involves the isomers $CH_3C{\equiv}C^-$ and $\bar{C}H_2C{\equiv}CH$. We have been interested in synthesizing specific isomeric species in the gas phase to compare their basicity, electron affinity and reactivity. This specific generation can be difficult due to isomerization during proton abstraction and it can also be difficult due to the presence of more than one acidic site in the parent molecule. This is true even for a molecule as simple as methyl acetylene, $CH_3C{\equiv}CH$, where we have shown that proton abstraction generates both $C_3H_3^-$ ions mentioned above (*10*).

One method of specific ion generation which we have explored involves the synthesis of trimethylsilyl derivatives, $(CH_3)_3SiR$. The gas phase reaction of fluoride ion with these derivatives is exothermic for many R groups due to the high strength of the Si-F bond:

$$F^- + (CH_3)_3SiR \rightarrow R^- + (CH_3)_3SiF \quad (24)$$

We have carried out these reactions for a variety of trimethylsilyl derivatives and have found many of the reactions to be efficient (*11*). In particular we have produced the two isomers of $C_3H_3^-$:

$$F^- + (CH_3)_3SiC{\equiv}CCH_3 \rightarrow {}^-C{\equiv}CCH_3 + (CH_3)_3SiF \quad (25)$$

$$F^- + (CH_3)_3SiCH_2C{\equiv}CH \rightarrow {}^-CH_2C{\equiv}CH + (CH_3)_3SiF \quad (26)$$

To demonstrate that two distinct isomeric species were indeed present, we carried out reactions of $C_3H_3^-$ with molecular oxygen. The mixture of ions formed by proton abstraction from $CH_3C{\equiv}CH$ gave curved kinetic plots indicating the presence of two species. The ions generated from each of the silanes [Eqs. (25) and (26)] gave linear semilogarithmic decay plots upon reaction with O_2, indicative of one species of ion; the reactivity of $CH_3C{\equiv}C^-$ and $HC{\equiv}CCH_2^-$ differed by a factor of seven, with the methyl acetylide ion being less reactive. Therefore, two distinct isomeric $C_3H_3^-$ ions were generated.

In conclusion, the flowing afterglow technique can provide important fundamental data on the reactions of organic negative ions which can be useful in negative ion chemical ionization mass spectrometry. In particular, the reactions of carbanions with both triplet and singlet molecular oxygen can serve as a valuable probe of ionic structures.

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