

Conclusions

A variety of anions were found to react with dimethyl disulfide, including all anions examined that are more basic than methanethiolate. In addition, sulfur nucleophiles slightly less basic than thiomethoxide were observed to undergo slow thiolate/disulfide interchange reactions with dimethyl disulfide, but anions less basic than HS^- reacted too slowly to give observed reaction products. Two bimolecular reaction pathways were found to account for all the primary reaction products: substitution at sulfur and elimination across the carbon-sulfur bond. Each of these two pathways can give more than one subsequent ion product. No evidence was found for an ion that would correspond to deprotonated dimethyl disulfide, and no evidence was found for carbon-centered substitution processes in the reactions examined. Nucleophilic displacement is thus an easier process at sulfur centers as compared to carbon centers. The primary factor in determining whether an anion gave sulfur substitution products or elimination products is the structure of the anion and not the energetics. Anionic bases of similar base strength (and similar reaction energetics), but of dissimilar structures, gave markedly different product distributions. Anions at least as basic as methoxide and in which the charge is localized preferred to react by elimination,

while delocalized carbanions of similar basicity strongly preferred substitution at sulfur (e.g., compare hydroxide to allyl anion and methoxide to benzyl anion). With anions less basic than methoxide, no evidence was found for elimination, which was interpreted to be due to the energetically unfavorable initial proton abstraction, even though the ultimate product (the rearranged thiolate ion) was exothermic or at least thermoneutral with respect to starting materials. Thus, when considering the competition between elimination and substitution, one needs to consider additional factors besides energetics. Hydroxide prefers elimination while allyl anion prefers substitution, at least in the reactions of dimethyl disulfide. These data on the intrinsic reactivity of anions with a model disulfide provide clear new insight into the fundamental chemical behavior of molecules containing sulfur-sulfur linkages.

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Registry No. Me_2S , 624-92-0; H_2N^- , 17655-31-1; HO^- , 14280-30-9; $\text{CH}_2=\text{CHCH}_2^-$, 1724-46-5; CH_3O^- , 3315-60-4; PhC^-HCH_3 , 13822-53-2; $\text{CH}_3\text{COCH}_2^-$, 24262-31-5; CH_2NO_2^- , 18137-96-7; CH_2CN^- , 21438-99-3.

Gas-Phase Ion-Molecule Reactions of the Nitric Oxide Anion

Elizabeth Rinden,[†] M. Matti Maricq,^{*,†} and Joseph J. Grabowski^{*,†}

Contribution from the Departments of Chemistry, Brown University, Providence, Rhode Island 02912, and Harvard University, Cambridge, Massachusetts 02138. Received June 28, 1988

Abstract: The chemical reactivity of nitric oxide anion (NO^-) with a variety of organic neutrals at ambient energies and in argon bath gas has been probed using the flowing afterglow technique. The reactions fall into four main classes: electron transfer, dissociative electron transfer and/or displacement, collisional detachment, and clustering. Electron transfer can occur when the neutral reactant possesses a positive electron affinity greater than the electron affinity of NO^\bullet , but does not always do so. Bimolecular substitution at sulfur is shown to occur with dimethyl disulfide, but for other substrates, distinguishing between displacement and dissociative electron transfer is not possible. Collisional detachment is the exclusive reaction channel observed for a few of the molecules examined and occurs to some extent with many of the neutrals tested. Cluster ion formation between NO^- and a number of the reactant neutrals which possess permanent dipole moments is observed. Additional pathways were observed for several of the neutrals examined. The collected observations are discussed in light of the general theory of ion-molecule reactions.

Nitric oxide has one of the smallest positive electron affinities known¹ ($\text{EA}[\text{NO}^\bullet] = 0.024 \text{ eV}$ or 0.55 kcal/mol). The binding energy of NO^- is so small that a significant fraction of the thermal collisions with gas molecules at room temperature contains sufficient energy to detach an electron.² Even though the rate coefficient for collisional detachment of NO^- by helium is small³ ($k_{\text{obs}} = 2.4 \times 10^{-13} \text{ cm}^3/\text{s}$; $k_{\text{obs}}/k_{\text{coll}} = 0.0004$), there are enough collisions between NO^- and the helium present at 0.3 Torr in most flowing afterglow (FA) experiments to ensure that the net probability of collisional detachment is near unity.

A number of years ago, Fehsenfeld and co-workers⁴ discovered that when argon is used in place of helium in a flowing afterglow,

a significant fraction of the NO^- ions survive the viscous flow through the reaction region of the apparatus and are readily detected. McFarland and colleagues³ took advantage of the

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(2) The electron binding energy of nitric oxide is less than kT at room temperature; at 300 K, $kT = 208.5 \text{ cm}^{-1}$, whereas 0.024 eV is equivalent to 193.6 cm^{-1} .

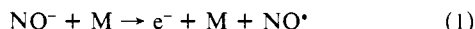
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[†]Brown University.

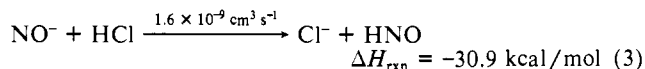
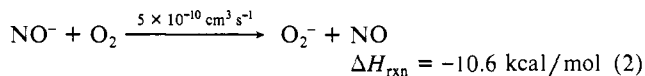
[†]Harvard University.

relative stability of NO^- in argon to measure collisional detachment rate coefficients of the type shown in eq 1 (for M equal to He, Ne, H_2 , CO, NO^* , CO_2 , N_2O , and NH_3) at temperatures ranging from 193 to 506 K.



The results of their study show that collisional detachment rate constants are largest for polyatomics containing low vibrational frequencies (NH_3 , N_2O , CO_2), while those for the atoms (He, Ne) and diatomic molecules possessing high vibrational frequencies (H_2 , CO) are relatively smaller. Marx and co-workers⁵ estimate that, at 285 K, detachment of NO^- by argon has a rate coefficient that is less than $1 \times 10^{-14} \text{ cm}^3/\text{s}$.

NO^- has been shown to undergo processes besides collisional detachment when appropriate neutral reactants are used in room-temperature investigations. Fast electron transfer is observed^{3,4} between NO^- and O_2 (eq 2), while quantitative chloride production⁶ is the result of the reaction of NO^- with HCl (eq 3).



As we show below, however, this represents only a small fraction of the chemistry of the NO^- anion.

Driven in part by the insight into the thermochemistry and dynamics of chemical processes in solution afforded by direct study of analogous phenomena in the absence of solvent, counterions, and aggregates, considerable attention has been paid to gas-phase, organic, anion-molecule reactions. While there have been numerous elegant studies of various organic reactions involving gas-phase anions, much less effort has been addressed to the role of electron transfer in such processes.⁷ Considerable effort thus far has been spent in the study of negative ion electron-transfer equilibria, a process that provides electron affinities of stable organic molecular anions.⁸ The chemical reactivity of a few, relatively weakly bound anions have been examined; the allyl ion is often used as a prototypical anion in gas-phase studies⁹ ($\text{EA}[\text{CH}_2=\text{CHCH}_2] = 0.357 \pm 0.015 \text{ eV}$),¹⁰ and the molecular oxygen anion has been found to be nucleophilic¹¹ in the gas phase ($\text{EA}[\text{O}_2] = 0.440 \pm 0.008$).¹² For the most part, however, direct electron transfer or processes instigated by electron transfer have received relatively little attention.

This paper examines the reactivity of NO^- in the collision-dominated environment of the flowing afterglow at room temperature. The prospect of using electron transfer from NO^- to synthesize other weakly bound anions provided impetus for the experiments reported herein. Toward this end, we report our examinations of the reactivity of NO^- with a series of organic molecules having a wide range of electron affinities and representing a variety of functional groups. Our findings reveal that NO^- shows a rich and varied chemistry, perhaps surprisingly so, in addition to the expected electron-transfer reactions. We find

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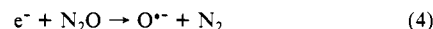
that four types of processes dominate how NO^- interacts with many molecules: electron transfer, dissociative electron transfer and/or displacement, collisional detachment, and cluster ion formation. Electron transfer occurs only with a fraction of reactant molecules for which this process is energetically allowed. Collisional detachment is the exclusive process for some of the molecules examined and occurs to some extent for a large number of species. Some of the reactants show a surprising tendency to form cluster ions with NO^- . We also report findings of some unusual chemistry which does not fall into the above four categories: the reactions of NO^- with acetaldehyde and di-*tert*-butyl peroxide.

The remainder of this paper is divided as follows. We present next a brief review of the flowing afterglow technique. In this section we also describe how we generate the NO^- reactant and how we ensure that our results are not obfuscated by interfering reactions due to the precursor used in forming the NO^- . Subsequently, we present the results obtained from the reaction of NO^- with a variety of reactant molecules, organized by the functionality of the reactant species. Our interpretation of the data and the reaction mechanisms involved are then presented in the Discussion section.

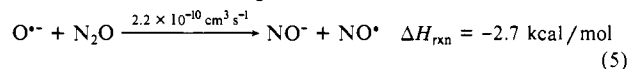
Experimental Section

The flowing afterglow technique (FA) is well documented;¹³ the Harvard University apparatus used for this work is described in detail elsewhere.¹⁴ The FA consists of three regions: ion source, reaction tube, and detector. A regulated, fast flow of buffer gas (argon, for these studies), introduced at the ion source, is pumped through the apparatus by a mechanical booster system. The buffer gas (total pressure of 0.20 Torr) serves to thermally equilibrate the reactants with the apparatus walls (300 K) through collisions and to carry the ions from the source, through the reaction region and either to the detector or out of the instrument. A precursor gas, admitted as a small percentage of the buffer gas flow, is ionized by electrons emitted from a thoriated iridium ribbon filament biased at -30 V with respect to a grounded acceleration grid and operated in constant emission current mode (0.025 mA). Either the first formed ion (e.g., O^+), or another reactive ion synthesized from it (e.g., NO^*), is examined in the reaction region (a 1-m long by 7.6-cm diameter flow tube) which extends from the source to the detector. At the terminus of the reaction region, the majority of the flow tube contents are removed from the system while the ions are sampled through a 1-mm molybdenum orifice located at the apex of a blunted 120° nosecone. The sampled ions enter a differentially pumped, high-vacuum chamber where they are mass analyzed by a quadrupole mass filter, detected by a conversion dynode electron multiplier, and counted via standard pulse-counting techniques.

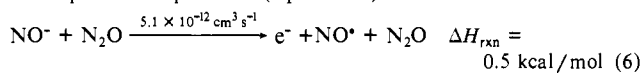
Production of the nitric oxide anion is accomplished by a well-known, two-step process. The first step¹⁵ involves dissociative electron attachment to nitrous oxide:



In a second step,^{3,5,6,15} the O^* ion is allowed to react with a second molecule of nitrous oxide to give NO^- :



Achievement of usable NO^- signals requires a delicate balance between production processes (eq 4 and 5) and collisional detachment:³



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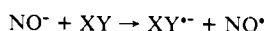
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Table I. Summary of Results for the Room-Temperature Reactions of Neutrals with NO⁻ in 0.2 Torr of Argon

group	neutral	EA		Are products detected from . . . ? ^a			
		(eV) ^b	ref	ET	DET/S _N 2	CD	CL
carbonyl compounds	biacetyl	0.702	<i>c</i>	Y	N	N	N
	benzaldehyde	0.430 ± 0.005	<i>d, e</i>	Y	N	Y	N
	acetaldehyde ^f	-1.19 (v)	<i>g</i>	N	N	Y	Y
sulfur compounds	acetone	-1.51 (v)	<i>g</i>	N	N	Y	Y
	sulfur dioxide	1.110 ± 0.006	<i>h</i>	Y	N	N	N
	carbon disulfide	0.60 ± 0.09	<i>i</i>	Y	N	N	N
	dimethyl disulfide	≥0.024; ≤0.440	this work	Y	Y	N	N
aromatic compounds	dimethyl sulfoxide			N	N	Y	Y
	nitrobenzene	0.97	<i>c, c</i>	Y	N	N	N
	benzotrile	0.239 ± 0.005	<i>d, e</i>	N	N	Y	Y
	pyridine	-0.62 ± 0.05 (v)	<i>j</i>	N	N	Y	Y
halides and pseudo-halides	benzene	-1.14 ± 0.05 (v)	<i>j</i>	N	N	Y	N
	carbon tetrachloride	2.0 ± 0.2	<i>k</i>	N	Y	N	N
	nitromethane	0.44 + 0.10, -0.20	<i>l</i>	N	N	Y	N
	methyl iodide	0.2 ± 0.2 (v)	<i>m</i>	N	Y	N	N
miscellaneous:	acetonitrile	-2.84 (v)	<i>g</i>	N	N	Y	Y
	propylene	-1.99 (v)	<i>g</i>	N	N	Y	N
	isoprene			N	N	Y	N
	tetramethylsilane			N	N	Y	N
	water			N	N	Y	Y
	dioxygen	0.440 ± 0.008	<i>n</i>	Y	N	N	N
	<i>tert</i> -butyl peroxide ^f			N	Y	N	N

^aET = electron transfer; DET/S_N2 = dissociative electron transfer and/or nucleophilic substitution (both give the same ionic product); CD = collisional detachment; CL = adduct formation (cluster). Y = yes, indicating the process is at least 1% of all reactive pathways for that neutral, and N = no evidence of reaction was observed. ^bThe electron affinities are adiabatic unless indicated as vertical (v). Error bars are indicated when available. ^cReference 8e. ^dReference 17. ^eReference 18. ^fOther products also detected; see text for details. ^gReference 19. ^hReference 20. ⁱReference 21. ^jReference 22. ^kReference 23. ^lReference 24. ^mReference 25. ⁿReference 12.

Scheme I. Electron Transfer



Addition of too much nitrous oxide quenches the NO⁻ signal; addition of too little nitrous oxide results in the atomic oxygen anion still being present when the reactions of NO⁻ are examined. To simplify data analysis we ensure that all of the O⁻ is quenched by nitrous oxide prior to neutral reagent addition by adding acetonitrile to the flow tube. Acetonitrile rapidly and distinctly reacts with the atomic oxygen anion.¹⁴ All the results herein were collected under conditions where the acetonitrile test described above indicated that no atomic oxygen anion was present when the reactions of NO⁻ were being examined.

Dioxygen is known^{3,4} to undergo fast electron transfer with NO⁻ (eq 2) providing both an anion whose reaction products can complicate interpretation of the NO⁻ chemistry and a route for loss of NO⁻. We minimize the O₂⁻ impurity signal (typically 10% of the NO⁻ signal) by using ultrahigh purity nitrous oxide (Scientific Gas Products, 99.99% purity) and prepurified grade argon (Medical-Technical Gases, 99.998% purity, containing <5 ppm of O₂). In addition, the argon is passed through a cartridge which reduces dioxygen to a level of <0.1 ppm by chemisorption on a highly active, supported metallic surface (Oxisorb I).

Some of the neutral reactants in this study are very sensitive to the presence of an O₂⁻ impurity; hence it is important to know what product ions might arise from this impurity. A separate study is used to identify products of reactions with O₂⁻. This information allows us to deduce which product ions in our NO⁻ experiments arise from reactions with NO⁻ and which arise from O₂⁻ impurity.

The presence of the O₂⁻ impurity is sometimes beneficial. If, for a particular reagent, the NO⁻ signal is decreased significantly more than the O₂⁻ signal, but the decrease cannot be accounted for by an obvious product ion, then we interpret this to indicate collisional detachment of NO⁻. The usual electron scavenging techniques (e.g., adding SF₆) are not useful here because of the fast reactions of NO⁻ with the scavenger.¹⁶

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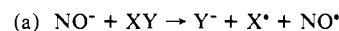
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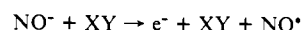
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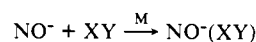
Scheme II. Dissociative Electron Transfer (IIa) and Displacement (IIb)



Scheme III. Collisional Detachment



Scheme IV. Adduct Formation



Results

In the following sections we present the results of a series of room-temperature investigations in which NO⁻ was allowed to react with a variety of neutral molecules. We have divided the neutrals examined into a series of classes; the molecules assigned to each class and their electron affinities are shown in Table I. In general, we find that NO⁻ reacts with any given neutral by way of one or more of four channels: electron transfer, dissociative electron transfer and/or displacement, collisional detachment, and adduct formation. These channels are described by Schemes I-IV. A summary of the results of the neutrals examined is given in Table I.

A fifth reaction pathway, that of NO⁻ acting as a Brønsted base, is not possible for most of the neutrals examined since HNO is more acidic than almost all of the neutrals listed in Table I ($\Delta H_{\text{acid}}(\text{HNO}) = 362.9 \pm 2.3 \text{ kcal/mol}$).²⁶ There are two possible exceptions to this latter statement. Nitromethane is more acidic than HNO ($\Delta H_{\text{acid}}(\text{CH}_3\text{NO}_2) = 356.4 \pm 2.9 \text{ kcal/mol}$);²⁶ however, no proton transfer is found in the reaction of NO⁻ with CH₃NO₂. The second possible exception is biacetyl, for which the gas-phase

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acidity has not been reported.²⁷ We observed no proton transfer in the reaction of NO⁻ with biacetyl.

Electron Transfer (Scheme I). For electron transfer to occur at a rapid rate, the minimum requirement is for an exothermic reaction which stipulates that the electron affinity of the neutral be greater than the electron affinity of NO⁻.

Dissociative Electron Transfer (DET) and Displacement (Scheme II). Dissociative electron transfer can be envisioned as charge transfer followed by dissociation. The ion product from dissociative electron transfer is often the same as that formed by a substitution reaction (S_N2), albeit with different neutral products.

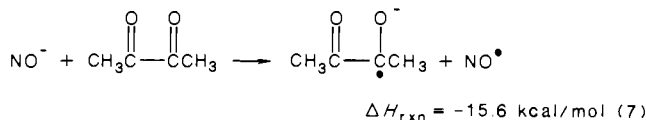
Collisional Detachment (Scheme III). The binding energy of the extra electron in NO⁻ is sufficiently small (0.55 kcal/mol) that a sizable fraction of collisions at 300 K may be energetic enough to cause detachment.² This process cannot be observed directly owing to the lack of a product ion. It is inferred from a loss of NO⁻ without a concomitant appearance of a sufficient number of product ions. However, it is possible that a collisional-detachment channel which accounts for only 5% of the overall reactant ion loss might go undetected.

Clustering (Scheme IV). Adduct formation is presumably a termolecular reaction wherein the argon acts as a third body to remove energy through collisions. It is known that argon exhibits termolecular stabilization rate coefficients that are a factor of 2 to 3 larger than those typically observed for helium.²⁸

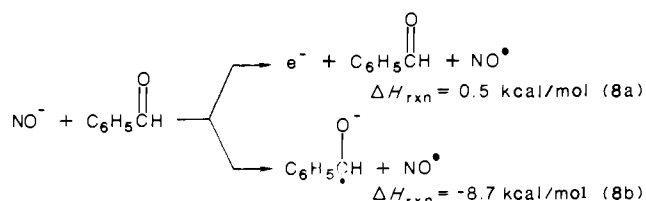
In addition to the four channels mentioned above, a couple of the molecules (i.e., acetaldehyde and di-*tert*-butyl peroxide) display additional chemistry which will be described below. While we have not measured absolute rate coefficients for any reaction reported in this work, we report qualitative observations on the rates; "fast" is meant to indicate that the reaction is on the order of 1% efficient or better, while "slow" indicates that products are observed in something less than 1 out of 100 collisions.

In the sections below, reaction schemes in which a product is shown within brackets signify that its structure is unknown. Only ions are detected; thus, neutral products which cannot be unambiguously deduced are contained within brackets. Reaction enthalpies are given for channels when there is sufficient information in the literature to calculate them. (Only reactions whose enthalpies are less than a few kcal/mol occur on a fast enough time scale for us to observe their products). Collisional-detachment reactions are shown when this type of reaction predominates. Otherwise, the presence of collisional detachment is revealed in the text and Table I.

Carbonyl Compounds. The reaction of NO⁻ with biacetyl is a rapid process that yields exclusively the molecular anion of biacetyl (eq 7) which presumably is the ketyl anion radical. This fast charge transfer has a large thermodynamic driving force since the electron affinity of biacetyl (0.702 eV) is considerably larger than the electron affinity of nitric oxide:



Benzaldehyde also is observed to undergo electron transfer with NO⁻ (eq 8b). In addition to electron transfer, it is apparent that

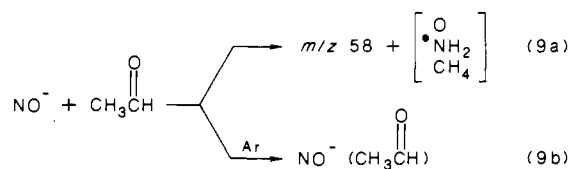


(27) An estimate of the acidity of biacetyl based upon observation of some proton abstraction by O₂⁻ has appeared in ref 11. However, in 0.2 Torr of argon, we find that neither NO⁻ nor O₂⁻ appears to abstract a proton from biacetyl; the only product we found from O₂⁻ with biacetyl in argon is the cluster ion.

(28) Ikezoe, Y.; Matsuoka, S.; Takebe, M.; Viggiano, A. *Gas Phase Ion-Molecule Reaction Rate Constants Through 1986*; Mass Spectroscopy Society of Japan: Tokyo, 1987.

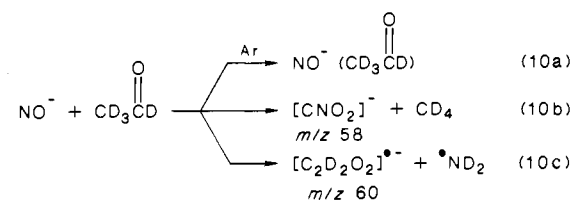
there is some NO⁻ signal loss, implying that a collisional-detachment process is also occurring. As with biacetyl, the observance of a significant electron-transfer channel for benzaldehyde is in accord with the larger electron affinity of PhCHO than that of NO⁻.

Two product ions are observed from the reaction of NO⁻ with acetaldehyde: a predominant ion at *m/z* 58 (eq 9a) and the adduct



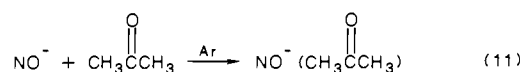
ion at *m/z* 74 (eq 9b). In addition, the sum of the two product ions does not fully account for the initial NO⁻ signal, implying that collisional detachment of NO⁻ by acetaldehyde is also occurring.

In eq 9a the possible neutral products for the channel forming the *m/z* 58 ion are shown in brackets. To obtain more information about the identity of the *m/z* 58 ion, we examined the reaction of NO⁻ with acetaldehyde-*d*₄. As shown in eq 10 NO⁻ reacts with



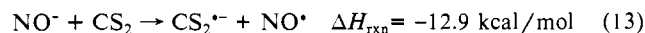
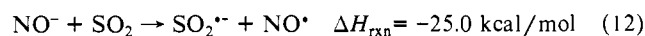
CD₃CDO to give the adduct and *m/z* 58 ions as did the protio compound. In addition a new ion at *m/z* 60 appears, which has about twice the intensity as the *m/z* 58 ion. The combination of acetaldehyde and acetaldehyde-*d*₄ experiments indicates that the *m/z* 58 ion in the protio case is most likely a mixture of [CNO₂]⁻ and [C₂H₂O₂]⁻. No evidence was found for a molecular anion of acetaldehyde.

When NO⁻ is allowed to react with acetone, slow reaction takes place and the only observed, primary ion product is the adduct at *m/z* 88 (eq 11). However, acetone also appears to collisionally

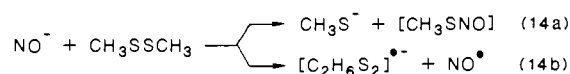


detach NO⁻. The structure of the adduct may be thought of as a cluster ion because, in a separate experiment, it is found to undergo slow solvent switching with added water. No evidence of the existence of an acetone molecular anion was found.

Sulfur Compounds. Both sulfur dioxide and carbon disulfide possess significantly positive electron affinities and, indeed, are observed to undergo fast, exclusive electron transfer with NO⁻ (eq 12 and 13).



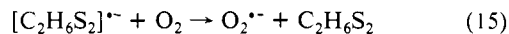
When NO⁻ is allowed to react with dimethyl disulfide, the major product ion observed is *m/z* 47 (eq 14a), CH₃S⁻, and a minor



product is found at *m/z* 94 which corresponds to the molecular anion resulting from charge transfer (eq 14b). As with sulfur dioxide and carbon disulfide, no evidence for collisional detachment of NO⁻ by dimethyl disulfide is found.

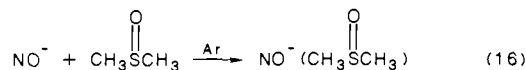
In order to elucidate the structure of the product anion observed at *m/z* 94 from the reaction of NO⁻ with dimethyl disulfide, it was allowed to react with a number of reagents. For example, the *m/z* 94 ion produced above was *not* observed to react with

methanol, 2,2,2-trifluoroethanol, or methanethiol. However, the m/z 94 ion was observed to undergo fast, quantitative electron transfer to dioxygen:



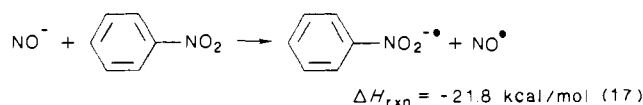
These data suggest that the m/z 94 ion is the molecular anion of dimethyl disulfide and not a cluster ion of the methyl thiolate anion solvated by the thiomethoxy radical or thioformaldehyde negative ion solvated by methanethiol or NOS_2^- . Our interpretation of the experimental observations suggests that the electron affinity of dimethyl disulfide is 0.23 ± 0.21 eV. This is based on the fact that NO^- ($\text{EA}(\text{NO}^*) = 0.024$ eV)^{1a} reacts with dimethyl disulfide to give a m/z 94, and that this ion readily transfers an electron to O_2 ($\text{EA}(\text{O}_2) = 0.440$ eV).¹²

Dimethyl sulfoxide is observed to react with NO^- to yield the cluster ion in a fairly rapid process (eq 16). Unlike the other



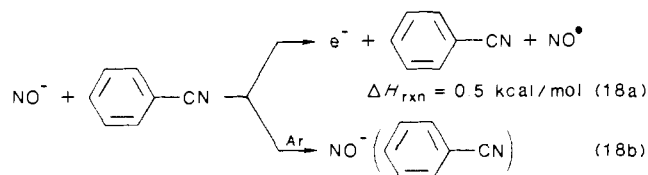
three sulfur compounds examined, dimethyl sulfoxide does not yield detectable amounts of the molecular anion. Finally some collisional detachment is probably taking place as the minor channel.

Aromatic Molecules. Nitrobenzene undergoes fast electron transfer with NO^- (eq 17) and this is the only process detected.



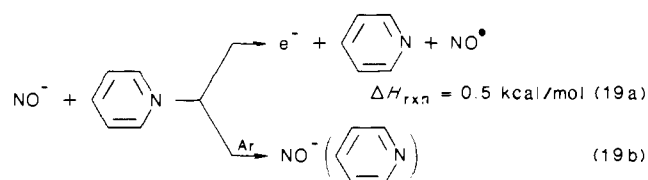
There is no evidence to suggest that collisional detachment of the NO^- is occurring.

Of the other aromatic compounds examined, benzonitrile is the only compound in addition to nitrobenzene to have a known positive electron affinity. When NO^- is allowed to react with benzonitrile, the only product ion detected is the cluster ion (eq 18b); the primary process of the NO^- and PhCN reaction appears

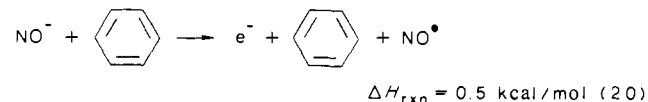


to be collisional detachment. The overall rate of disappearance of NO^- is slow for this reaction.

Pyridine displays a behavior with NO^- that is very similar to that of benzonitrile. Only slow reaction is observed, forming a cluster product ion which is detected (eq 19b), while the major channel is collisional detachment (eq 19a).

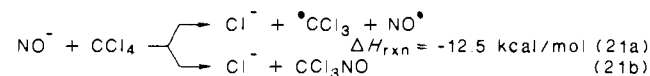


Addition of benzene to a flow tube of NO^- results in the slow disappearance of the NO^- signal with no new product ions appearing. Thus, it appears that for benzene collisional detachment is the only significant process.



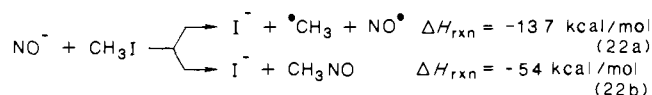
Halides/Pseudo-Halides. Carbon tetrachloride has been reported²³ to have a strongly bound molecular anion, $\text{EA}(\text{CCl}_4) = 2.0 \pm 0.2$ eV. When NO^- was allowed to react with CCl_4 under thermally equilibrated conditions (300 K in a 0.20 Torr argon

environment), fast reaction was observed to give chloride ions as the exclusive channel (i.e., there appears to be no collisional detachment).



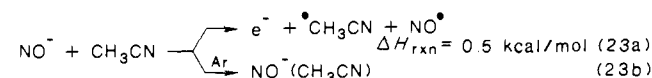
Nitromethane is another small molecule which has been reported²⁴ to possess a bound molecular anion, $\text{EA}(\text{CH}_3\text{NO}_2) = 0.44 \pm 0.20$ eV. Unlike carbon tetrachloride and methyl iodide, nitromethane appears to exhibit exclusively fast collisional detachment in its reaction with NO^- . Unfortunately, we cannot completely rule out production of a small amount (no more than 5%) of NO_2^- , although it is unlikely. The ambiguity is due to the presence of the small O_2^{*-} signal which contaminates our NO^- signal; we have shown that O_2^{*-} rapidly reacts with nitromethane, giving NO_2^- as a principal product ion.

Methyl iodide is reported²⁵ to have a much weaker bound molecular anion, $\text{EA}(\text{CH}_3\text{I}) = 0.2 \pm 0.2$ eV, than carbon tetrachloride. However, in direct analogy to the carbon tetrachloride reaction the sole process occurring during the reaction of NO^- with methyl iodide is rapid formation of iodide, by either dissociative electron transfer (eq 22a) or displacement (eq 22b).

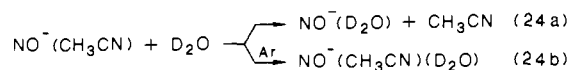


In both the carbon tetrachloride and methyl iodide reactions no evidence for production of a long-lived (at least 5 ms) molecular anion was found. Because we are unable to detect the neutral products of a reaction, we cannot experimentally distinguish between the two possible halide-producing channels.

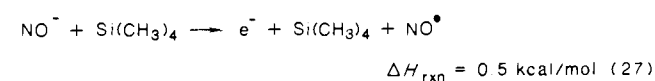
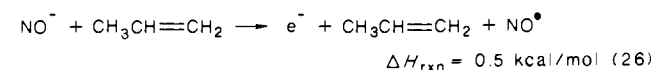
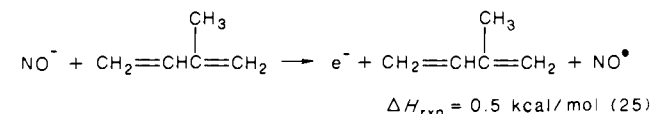
Acetonitrile reacts with NO^- by way of competitive collisional detachment (principal process) and cluster formation:



O_2^{*-} is known to react with acetonitrile in helium buffer gas with a moderate rate coefficient²⁹ ($k = 3.7 \times 10^{-11}$ cm³/s at 0.40 Torr) to give the cluster ion exclusively. Our present studies indicate that NO^- has a considerably larger rate coefficient for reaction with acetonitrile than does O_2^{*-} . The nitric oxide anion-acetonitrile cluster undergoes only slow reaction with added D_2O in a 0.20 Torr argon environment to give somewhat more solvent switching (eq 24a) than further clustering (eq 24b):



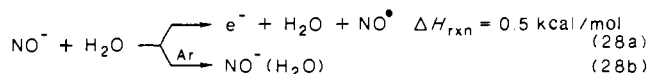
Miscellaneous. The three hydrocarbons examined in this study (benzene, propylene, isoprene) and tetramethylsilane, all reveal slow collisional detachment as the exclusive process with NO^- (eq 20, 25-27).



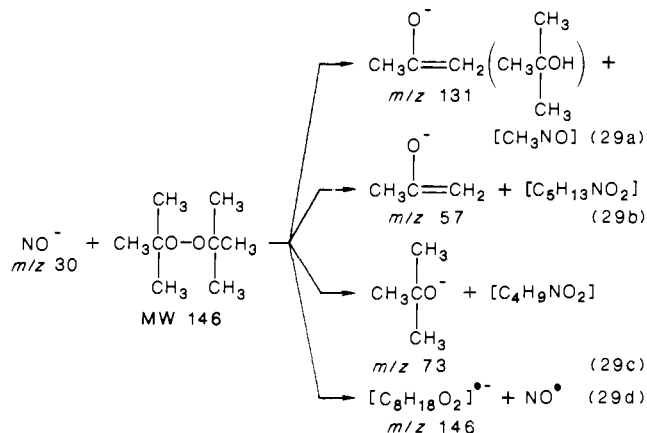
Water is also observed to react slowly, albeit completely, with NO^- yielding predominantly collisional-detachment products (eq

(29) Viggiano, A. A.; Paulson, J. F. In *Swarms of Ions and Electrons in Gases*; Lindinger, W.; Mark, T. D.; Howorka, F., Eds.; Springer-Verlag: New York, 1984; pp 218-240.

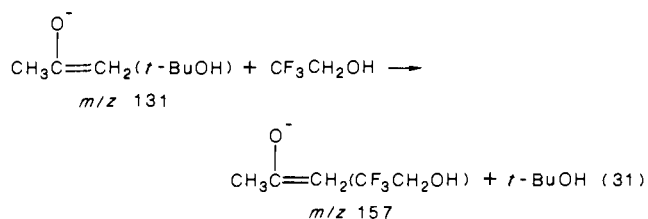
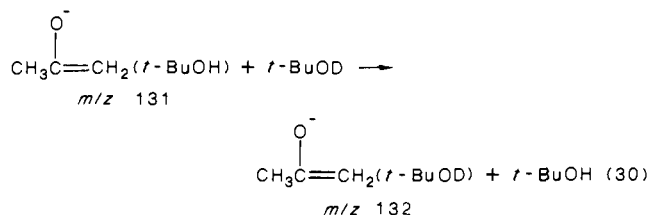
28a), although a trace of the $\text{NO}^-(\text{H}_2\text{O})$ cluster ion (eq 28b) is also observed.



The last molecule examined here is di-*tert*-butyl peroxide, a species undergoing in-depth studies in our lab. When NO^- is allowed to react with di-*tert*-butyl peroxide, four product ions are observed which appear to account for all reaction channels (eq 29). By far, the principal product ion from NO^- and di-*tert*-butyl



peroxide is the ion at m/z 131 to which we have assigned the structure of acetone enolate solvated by *tert*-butyl alcohol. This structural assignment for m/z 131 is based upon the fast solvent switching reactions observed with both *tert*-butyl alcohol-*O-d* (eq 30) and 2,2,2-trifluoroethanol (eq 31). Further support for the



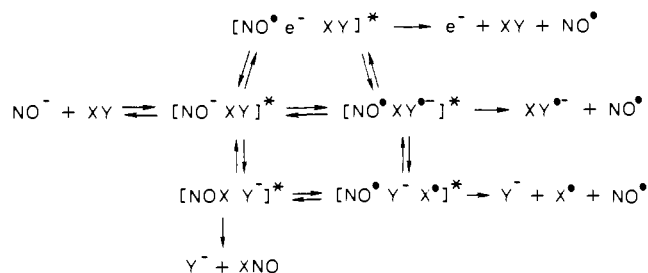
assignment comes from the observation of additional slow H/D exchange of the m/z 132 ion upon prolonged exposure to *t*-BuOD (three additional exchanges are observed; the last two exchanges are not observed owing to kinetic limitations).³⁰

The m/z 146 ion produced in the reaction of NO^- with di-*tert*-butyl peroxide was also observed to undergo solvent-switching reactions with both *tert*-butyl alcohol-*O-d* and 2,2,2-trifluoroethanol, leading us to suggest that it is the cluster ion consisting of *tert*-butoxide solvated by the *tert*-butoxy radical. Additional support for such an assignment comes from the observed *tert*-butoxide product (eq 29c).

Discussion

At a fundamental level, one can consider the generalized reaction scheme for describing the interaction of NO^- with a neutral molecule shown in Scheme V. In this scheme, NO^- and a neutral

Scheme V. Generalized Reaction Scheme for the Interaction of NO^- with Neutral XY^a



^aFor clarity the termolecular stabilization channels have been omitted. The brackets indicate distinct ion-neutral complexes; the asterisks indicate that the ion-neutral complex contains excess energy.

molecule, XY , enter into a collision complex depicted within brackets, and shown with an asterisk to indicate that the complex contains excess energy. The collision complex can conceivably exist in discrete chemical forms as discussed below. The excess energy in any complex arises in part from the electrostatic attraction between NO^- and XY which is typically in the range of 10 to 20 kcal/mol. The existence of the bracketed, intermediate complex, in any form, is speculative, although the existence of observed, stable cluster ions for many of the reactions studied in this work indicate that at least some of the intermediate complexes in Scheme V occur.

Assuming that the initially formed complex in Scheme V is $[\text{NO}^- + \text{XY}]^*$, there are four possible pathways which it may take including dissociation back to reactants. The electron can transfer from NO^- to XY to form $[\text{NO}^\bullet + \text{XY}^\bullet]^*$ which may either dissociate to give the products of electron transfer or undergo rearrangement to create either of two further complexes: $[\text{NO}^\bullet + e^- + \text{XY}]^*$ or $[\text{NO}^\bullet + \text{Y}^- + \text{X}^\bullet]^*$. A third reaction pathway of our first formed complex is nucleophilic displacement to give $[\text{ONX} + \text{Y}^-]^*$. The newly formed $[\text{NOX} + \text{Y}^-]^*$ complex may dissociate to yield the products of an $\text{S}_{\text{N}}2$ displacement reaction, $\text{Y}^- + \text{XNO}$, or it may break a bond to form $[\text{NO}^\bullet + \text{Y}^- + \text{X}^\bullet]^*$. The fourth pathway of the first-formed complex, $[\text{NO}^- + \text{XY}]^*$, is collisional detachment via the intermediate $[\text{NO}^\bullet + e^- + \text{XY}]^*$. Unlike the previous pathways, which lead to experimentally observable ion products, collisional detachment can only be inferred by an otherwise unaccountable loss of NO^- signal.

If the second-formed ion-neutral complexes, $[\text{ONX} + \text{Y}^-]^*$ and $[\text{NO}^\bullet + \text{XY}^\bullet]^*$, undergo bond cleavage to form $[\text{NO}^\bullet + \text{X}^\bullet + \text{Y}^-]^*$, either by utilizing some of the excess energy available from ion-neutral interaction or the exothermicity released by rearrangements in their formation, the ultimate products will be those of dissociative electron transfer, $(\text{Y}^- + \text{X}^\bullet + \text{NO}^\bullet)$.

The generalized scheme shown in Scheme V is consistent with the data reported herein and with general ideas of room-temperature ion-molecule interactions.³³ In some situations one or more of the complexes shown in this scheme may not exist. For example, it is conceivable that in an electron-transfer reaction, the electron hops from NO^- to the neutral reactant without the necessity of forming an ion-dipole complex. With certain neutral reactants, NO^- exhibits both electron transfer and substitution products. It is possible that a direct mechanism is responsible for the charge transfer, whereas the substitution reaction proceeds via an intermediate complex. We next consider how the specific reaction results of this work are described within the generalized scheme of Scheme V.

Rapid and exclusive electron transfer from NO^- to biacetyl, sulfur dioxide, carbon disulfide, nitrobenzene, and dioxygen is

(30) H/D exchange of organic anions in the gas phase has been extensively studied (e.g., ref 31), and exchange involving gas-phase hydroxide-water or methoxide-methanol cluster ions are currently being examined (ref 32). We are not aware of any previous publication reporting H/D exchange of an organic ion which is part of a cluster ion.

(31) (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650-7653. (b) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565-2571. (c) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185-5192.

(32) DePuy, C. H., unpublished data.

(33) Ferguson, E. E. *Chem. Phys. Lett.* **1983**, *99*, 89-92.

observed. Each of the molecules has a positive, adiabatic electron affinity larger than that of NO^* (Table I), and none possess an exothermic dissociative electron transfer path. Therefore it is likely that these reactions follow the pathway via $[\text{NO}^* + \text{XY}^*]^*$ to produce electron-transfer products. The observation of charge transfer depends upon more than whether or not the reaction is exothermic since O_2^{*-} does not charge transfer to biacetyl either in argon buffer (this work) or in helium buffer.¹¹ Benzaldehyde also undergoes electron transfer and also has only endothermic dissociative electron-transfer channels. However, benzaldehyde is different from the other molecules in that observed electron transfer is clearly in competition with collisional detachment. Both product channels for NO^- and benzaldehyde (electron transfer and collisional detachment) may arise via a common intermediate, $[\text{NO}^* + \text{PhCHO}^*]^*$. This common intermediate can dissociate to yield exclusively the molecular anion of benzaldehyde which is then subject to slow collisional detachment in the argon buffer gas. The observation of significant amounts of the molecular anion of benzaldehyde as well as the strong inference of collisional detachment suggests exclusive electron transfer from NO^- to PhCHO followed by a kinetically controlled, collisional-detachment process that has not reached completion.³⁴ While collisional detachment, by a room-temperature interaction of an anion with a 0.43-eV binding energy is expected to be very slow, the detachment rate can be significantly enhanced if the anion (i.e., benzaldehyde) is formed in a vibrationally excited state. The slow collisional detachment of the benzaldehyde molecular ion by argon is supported by the observation that added dinitrogen also collisionally detaches PhCHO^* .

The reaction between dimethyl disulfide and NO^- reveals two processes; the predominant reaction occurring between NO^- and CH_3SSCH_3 is production of the methyl thiolate anion, CH_3S^- , while electron transfer to yield the molecular ion is the minor pathway. One can envision that both of these products arise from the electron-transfer complex, $[\text{NO}^* \text{CH}_3\text{SSCH}_3^*]^*$, where there is competition between dissociation of the complex and cleavage of the disulfide bond followed by dissociation of the resulting complex. Alternatively, electron transfer may occur via a direct process while CH_3S^- production results from ion-dipole complexes (vide supra). It is also distinctly possible that the methyl thiolate anion arises from displacement on sulfur in dimethyl disulfide since a number of anions of similar basicity to NO^- are known to react via such processes.³⁵ As is apparent in this and other cases, distinguishing between displacement and dissociative electron transfer is not simple. Four of the molecules examined, dimethyl disulfide, carbon tetrachloride, methyl iodide, and di-*tert*-butyl peroxide, display products that could result from either dissociative electron transfer (DET) or nucleophilic substitution.

One approach for distinguishing between DET and $\text{S}_{\text{N}}2$ is to consider the energetics of displacement versus dissociative electron transfer. For a given $\text{NO}^- + \text{XY}$ reaction, the displacement channel will always be more exothermic than the dissociative electron-transfer channel by the amount of energy gained from forming the new bond (i.e., $\text{BDE}(\text{X}-\text{NO})$). For the dissociative electron-transfer channel to be exothermic, it is necessary for the energy gained upon transfer of the electron to be greater than the bond dissociation energy of the newly formed molecular anion (i.e., $\text{EA}[\text{XY}] - \text{EA}[\text{NO}^*] > \text{BDE}[\text{X}-\text{Y}^*]$). The dissociative electron transfer is also thermochemically allowed when the difference in electron binding energies of NO^- and the product anion is larger than the bond dissociation energy in the neutral (i.e., $\text{EA}[\text{Y}^*] - \text{EA}[\text{NO}^*] > \text{BDE}[\text{X}-\text{Y}]$). The criterion for the displacement reaction to be exothermic requires that the difference in electron affinities of NO^* and Y^* , plus the strength of the new $\text{X}-\text{NO}$ bond, be larger than the $\text{X}-\text{Y}$ homolytic bond strength (i.e., $\text{EA}[\text{Y}^*] - \text{EA}[\text{NO}^*] + \text{BDE}[\text{X}-\text{NO}] > \text{BDE}[\text{X}-\text{Y}]$).

Table II. Thermochemical Data Used in This Work^a

species	EA (eV)	ref	species	BDE (eV)	ref
CN^*	3.821	c	$\text{H}_3\text{C}-\text{CN}$	5.37	c
NO^*	0.024	b	$\text{H}_3\text{C}-\text{NO}$	1.75	e
			$\text{H}_3\text{C}-\text{NO}_2$	2.63	e
Cl^*	3.617	c	$\text{CH}_3\text{S}-\text{SCH}_3$	3.21	f
NO_2^*	2.275	c	$\text{H}_3\text{C}-\text{SSCH}_3$	2.47	f
CH_3S^*	1.861	c	$\text{Ph}-\text{CN}$	5.53	e
$(\text{CH}_3)_3\text{CO}^*$	1.912	c	$\text{H}_3\text{C}-\text{I}$	2.44	c
C_6H_5^*	0.90	c			
CH_3SS^*	1.757	d	$(\text{CH}_3)_3\text{CO}-\text{OC}(\text{CH}_3)_3$	1.65	c
I^*	3.0591	c	$\text{Cl}_3\text{C}-\text{Cl}$	3.05	c

^aSee Table I for the electron affinities of the neutrals examined in this work. ^bReference 1. ^cReference 36. ^dReference 37. ^eReference 38. ^fReference 39.

By utilizing the above criteria and the values in Table II, we can eliminate endothermic pathways from consideration. Of the four reactant molecules which show products that can result from either displacement or dissociative electron transfer, only CH_3SSCH_3 has endothermic DET channels. Thus the reaction of NO^- with dimethyl disulfide that produces CH_3S^- must be a displacement reaction.³⁵ In terms of the general reaction scheme shown in Scheme V, the important ion-neutral complex for the reaction of NO^- with dimethyl disulfide is likely to be $[\text{NO}^- \text{XY}]$; branching from this first-formed complex decides the amount of electron transfer versus substitution products ultimately found. We are unable to say anything definitive at this time about DET versus $\text{S}_{\text{N}}2$ for methyl iodide, carbon tetrachloride, or di-*tert*-butyl peroxide (both DET and $\text{S}_{\text{N}}2$ channels are exothermic for each of these three molecules), though one could argue that the dissociative electron-transfer path is most likely to be favored. The same energetic considerations for reaction thermochemistry show that nitromethane, acetonitrile, and benzonitrile do not undergo DET because this reaction is endothermic for each of these molecules. Although displacement reactions for both CH_3NO_2 and CH_3CN are thermochemically allowed, they are not observed experimentally. The lack of displacement products at carbon, even when highly exothermic, is one piece of circumstantial evidence that indicates DET is preferred over substitution for methyl iodide (for example). Both nitromethane and benzonitrile have positive electron affinities (Table I) although neither show products from electron transfer. Our results indicate either that the electron affinities of nitromethane and benzaldehyde cited in Table I are wrong (which seems unlikely to us) or there may be a barrier to exothermic electron transfer or that the electron-transfer product is born vibrationally excited and autodetaches. We are unable to distinguish between direct collisional detachment of NO^- by nitromethane or benzonitrile, and electron transfer followed by rapid and quantitative detachment of the new molecular anion by argon.

When a collision transfers a sufficient amount of energy to NO^- , the ion may lose an electron to the translational continuum. We believe that this reaction occurs to some extent with many of the reactant molecules studied. Molecules whose predominant reaction with NO^- is collisional detachment are propylene, isoprene, benzene, tetramethylsilane, acetonitrile, benzonitrile, pyridine, water, and nitromethane. The hydrocarbons all showed exclusive collisional detachment in accord with the knowledge that they do not possess bound molecular anions. For the other molecules which show collisional detachment, we often observe that cluster ion formation is in competition with collisional detachment if the molecule contains a dipole moment (i.e., the molecule can form a reasonably strong electrostatic bond). We are surprised by the "reluctance" of NO^- to undergo collisional detachment as evidenced by the many other channels observed when it reacts with neutral molecules.

(34) Hierl, P. M.; Ahrens, A. F.; Henchman, M.; Viggiano, A. A.; Paulson, J. F. *Int. J. Mass Spectrom. Ion Phys.* **1987**, *81*, 101-122.

(35) Grabowski, J. J.; Zhang, L. *J. Am. Chem. Soc.*, previous paper in this issue.

(36) *CRC Handbook of Chemistry and Physics*, 66th ed; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985.

(37) Moran, S.; Ellison, G. B. *J. Phys. Chem.* **1988**, *92*, 1794-1803.

(38) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

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Clustering of an ion with a neutral molecule, most often via a third-body stabilizing collision, is a well-known process; the exothermicity of a clustering reaction is defined by the ion-solvation energy. While measurements of many cluster ion bond strengths have been made,⁴⁰ very little is known about $\text{NO}^-(\text{XY})$ bond strengths. Recent photoelectron spectroscopy studies of Bowen and co-workers⁴¹ have shown that $\text{NO}^-(\text{N}_2\text{O})$ is characterized by an intact NO^- solvated by N_2O with an interaction energy of 4.6 kcal/mol. In our system, we have not observed $\text{NO}^-(\text{N}_2\text{O})$, presumably because only a minimum amount of N_2O is being added, and also because such a weakly bound solvated ion has an insufficient lifetime in our multicollision reaction chamber.³⁴ We do observe NO^- cluster ion products with acetaldehyde, acetone, dimethyl sulfoxide, benzonitrile, pyridine, acetonitrile, and water. All the molecules which exhibit clustering can be characterized as being polar molecules. Conversely, no cluster ion products are observed for the nonpolar, neutral molecules examined. We believe that all of the cluster ions are ion-neutral complexes bound by electrostatic interactions only (as opposed to covalent bonds) based on limited solvent-switching studies. The rather surprising observation of so many successful (presumably) termolecular reactions of NO^- in argon must be attributed to both slow collisional detachment processes and efficient three-body stabilization by argon.

An intriguing exception to expected clustering reactions is nitromethane for which only collisional detachment was observed. When O_2^{*-} was allowed to react with nitromethane in 0.20 Torr of argon, the $\text{O}_2^{*-}(\text{CH}_3\text{NO}_2)$ cluster ion is a major product (along with NO_2^-). In addition, cluster ions are observed between NO^- and all the other simple, polar, organic molecules (e.g., acetaldehyde, acetone, dimethyl sulfoxide, and acetonitrile). Whether the unique behavior observed for nitromethane is an indication that NO^- electron transfers to nitromethane upon every collision, but then the nitromethane molecular anion is efficiently collisionally detached or some other behavior occurs, is under active investigation.

Two of the molecules examined, acetaldehyde and di-*tert*-butyl peroxide, display chemistry other than that shown in Schemes I through IV, and several of the other reactions observed in this study require additional discussion. First, the reaction of NO^- with acetaldehyde is quite surprising, not in terms of the collisional detachment or cluster ion formation, the two processes which account for the majority of the reaction, but in terms of the formation of m/z 58. As shown by the results of NO^- plus CD_3CDO , m/z 58 in the all-protio case is most likely a mixture of two different ions. Additional studies are now being carried out to further enhance our understanding of how these ions are formed.

For di-*tert*-butyl peroxide it appears that the principal product from the reaction of NO^- is m/z 131, which we have shown to be acetone enolate solvated by *tert*-butyl alcohol. We envision the principal ion product as arising from a process that is initiated by dissociative electron transfer, forming *tert*-butoxide solvated by *tert*-butoxy radical, a trace of which is collisionally stabilized by the 0.2 Torr argon to give the ion observed at m/z 146. However, the principal process of the initially formed DET complex is fragmentation, giving rise to the m/z 131 ion. Fragmentation of *tert*-butoxy radical to a methyl radical is a well-known process.⁴² Such a concept is further supported by the observation of small amounts of acetone enolate and *tert*-butoxide. The acidities of acetone ($\Delta H^\circ_{\text{acid}}[\text{acetone}] = 369.1 \pm 2.6$ kcal/mol) and *tert*-butyl alcohol ($\Delta H^\circ_{\text{acid}}[t\text{-BuOH}] = 374.6 \pm 2.2$ kcal/mol) are sufficiently close to make such an explanation

plausible.²⁶ Additional studies with a variety of anions and di-*tert*-butyl peroxide shows that NO^- , the allyl anion, and O_2^{*-} exhibit unique behavior consistent with chemistry initiated by dissociative electron transfer.⁴³

Of the four carbonyl compounds examined, both biacetyl and benzaldehyde showed formation of ketyl radical anions, while acetone and acetaldehyde did not. The formation of ketyl radical anions by ion-molecule reactions cannot be predicted solely based on known relative electron affinities. As first reported by McDonald and co-workers¹¹ for helium buffer gas, and confirmed by us for argon buffer gas, O_2^{*-} does not charge transfer to biacetyl even though such a reaction is considerably exothermic. The slowness of charge transfer from O_2^{*-} may be due to O_2 being a ground-state triplet.

The results of the reaction between NO^- and methyl iodide or carbon tetrachloride are interesting. Both molecules have been reported to have bound molecular anions based on fast alkali beam reactions.^{23,25} For instance, at about 13 eV collision energy between CCl_4 molecules and a beam of potassium atoms, a yield of 0.4% CCl_4^{*-} is reported while Cl^- is the major ionic product (90.6%). The thermally equilibrated (300 K) reaction of NO^- with carbon tetrachloride is quite different, giving only Cl^- as a product ion. Similarly, methyl iodide reacts with NO^- to give solely the I^- ion. No evidence was found for stable molecular ions or other product ions (i.e., if such species exist, they are less than 0.1% of all products) for either carbon tetrachloride or methyl iodide. It seems surprising to us that a stable molecular anion would be formed in the high-energy alkali atom beam experiments, but not in our low-energy flowing afterglow apparatus. The difference may be due to the much longer lifetimes required for an ion to be detected in the flowing afterglow (ca. 5 ms) than in the high-energy beam experiments. However, there seems to be some question^{25b} in the case of methyl iodide as to whether it has a positive (vertical) electron affinity as reported.^{25a} Thus, from this study, it appears that the molecular anions of methyl iodide and carbon tetrachloride possess only small barriers (if any) to dissociation and that it is unlikely that they will be observed in a multicollision environment.

Conclusions

NO^- is observed to undergo a variety of reactions when allowed to interact with neutral molecules in the thermally equilibrated environment of the flowing afterglow. Exothermic electron transfer only sometimes predominates. For polar molecules which cannot undergo exothermic electron transfer, cluster ion formation, aided by the argon buffer gas, is a facile pathway. Dissociative electron transfer and/or displacement processes are also observed when allowed by thermochemistry. Displacement dominated over the electron-transfer reaction in the sole case where both reactions occurred (dimethyl disulfide). Ketyl radical anions were formed where the carbonyl compound contained radical stabilizing groups (biacetyl and benzaldehyde). Collisional detachment is only observed when electron transfer, dissociative electron transfer/displacement, and cluster ion formation are too slow. Since collisional detachment is always possible, we found no molecule that did not react with NO^- . Thus, the chemistry displayed by the closed-shell anion, NO^- , reacting with a series of stable, neutral molecules is rich and varied. Two aspects of this work invite immediate extension, that of the synthesis (and further reactivity) of ketyl radical anions by NO^- reactions, and elucidation of the novel and as yet, confusing chemistry shown by the reaction of NO^- with acetaldehyde.

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