Ion–Molecule Reactions of NO^+ with Organic Molecules by Ion Cyclotron Resonance Spectroscopy

Ashley D. Williamson and J. L. Beauchamp*[1]

Contribution No. 5019 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received December 13, 1974

Abstract: Ion cyclotron resonance techniques are used to study the reactions of NO^+ with various organic molecules in the gas phase. NO^+ reacts with acetaldehyde and isobutane by hydride transfer, yielding CH_3CO^+ and $(CH_3)_3C^+$, respectively. Association of NO^+ with an organic halide RX leads to the formation of a chemically activated species which may dissociate to the reactants or, when exothermic, to a nitrosyl halide XNO and a carbonium ion R^+ (halide transfer). In some cases the intermediate is also observed to eliminate HX to give an alkene, with NO^+ remaining bound to either species in the products. Transfer of NO^+ from these products to various π- and n-donor bases occurs readily. The activated complex formed by reaction of NO^+ with alcohols does not follow the pattern of the organic halide reactions, but decomposes instead by transfer of OH^- or an α hydride to NO^+. The important factor in reactions of NO^+ is its Lewis acid character.

Since the molecular ion of nitric oxide is isoelectronic with stable N_2 and CO, it is expected to be a species of low reactivity. However, several reactions of NO^+ have been reported in the literature. Most widely studied are termolecular association reactions of NO^+ with neutral molecules, including NO,[2] H_2O,[3] NH_3,[4] N_2,[5] O_2,[5] CO_2,[5] O_3,[6] CH_3OH,[7] and aromatic molecules.[8] In addition to association reactions, Einolf and Munson[9] report charge exchange from NO^+ to species with lower ionization energies under chemical ionization conditions. Hunt and Ryan[10] have also provided a preliminary account which suggests that NO^+ may be an interesting reagent ion for chemical ionization studies. Searles and Sieck[11] report hydride abstraction from alkanes, and note that this reaction is of considerable interest to radiation chemists, since nitric oxide is often used as a free radical[12] or charge scavenger.[13] Since appreciable amounts of NO^+ are formed in such experiments, further reactions of NO^+ might lead to incorrect inferences concerning radiolytic processes. This probable complication to the radiation chemist lends interest to a study of ion–molecule reactions of NO^+ with organic molecules, especially where heteroatom substituents establish a reactive center.

The interest in using NO^+ as a reagent ion for chemical ionization studies[9,10] is based on the observation that its reactivity is quite different from that of the majority of chemical ionization reagents, which are Brϕnsted acids (proton donors). As noted by Hunt and Ryan,[10] NO^+ acts as an electron acceptor, hydride abstracting agent, and electrophile, which are characteristic of Lewis acids. The chemical ionization studies to date[9,10] indicate that NO^+ causes a "soft" ionization, with very little fragmentation of the product ions.

At present we are conducting photoionization studies on the effects of internal energy on ion-molecule reactions.[14] Several factors make NO^+ an excellent candidate for such studies. Nitric oxide has a low ionization potential (9.25 eV) and a well characterized ionization efficiency curve;[15] measurements exist for the vibrational distribution of NO^+ formed in the electronic ground state by photoionization at selected wavelengths.[16] Moreover, NO^+ has triplet states which can be populated by photoionization[17] and may have significantly different reactivity from the singlet ground state. In this investigation we report observation of a variety of reactions of NO^+ with organic molecules using the techniques of ion cyclotron resonance spectroscopy (ICR). Some of the observed reactions are currently being investigated by the techniques of photoionization mass spectrometry.

Experimental Section

The principles and techniques of ICR have been described in detail elsewhere.[18,19] Experiments were performed on an instrument built in the Caltech shops, which is described in detail elsewhere.[20] All spectra were taken at ambient temperature. Reagent gases were introduced through separate inlet systems and leak valves. Partial pressures of each component were measured using a Schulz-Phelps ionization gauge. The ionization gauge was calibrated for each component against an MKS Baratron capacitance manometer as previously described.[21]

Ion storage studies were performed using the techniques of McMahon and Beauchamp.[19] Spectra were recorded in two modes. Mass spectra were obtained with a suitable delay time for reaction. This allowed identification of the ions present and permitted double resonance confirmation of reaction pathways.[18] Once these pathways were identified, the variation of ion abundance with time was determined and the data were analyzed to obtain rate constants. Studies were performed at low electron energy (10–15 eV) to minimize ionization of the reaction partner of NO^+. Low ionizing energies also suppress complications due to NO^+ triplet states having ionization thresholds above 15 eV. These states are probably metastable toward decay to the singlet ground state of the ion and energetic enough to induce dissociative charge exchange in many organic molecules, giving rise to fragment ions which might be mistaken for reaction products of ground state NO^+. This effect was noted at higher electron energies in some of our systems, indicating that caution should be exercised in interpretation of NO^+ reactions when higher ionizing energies are used.

Nitric oxide and isobutane were obtained from Matheson Gas Products, benzyl fluoride from Pierce Chemical Co., and 2,2-difluoropropane from Cationics, Inc. Isopropyl fluoride was prepared in our laboratories by Dr. John Y. Park from the reaction of AgF and isopropyl iodide and purified by gas chromatography. C_2D_5OH was prepared in our laboratories by Dr. T. B. McMahon by refluxing ethanol-d_6 with magnesium turnings. The resultant diethoxide salt was treated with water and the alcohol was distilled. The sample was purified by bulb-to-bulb distillation and found to be >99% pure by mass spectrometric analysis.[22] In the preparation of $(CD_3)_2CHCl$, acetone-d_6 was first reduced with lithium aluminum hydride in diethyl ether and the resulting $(CD_3)_2CHOH$ was distilled.[23] This alcohol was reacted with a zinc chloride-concentrated hydrochloric acid mixture.[24] The product $(CD_3)_2CHCl$ was distilled, washed with water, dried with calcium chloride, and found to be 90% isotopically pure by mass spectrometric analysis. The sample contained 10% of the d_5 compound, which did not hinder its use in our studies.

Results

Observed reactions are summarized in Table I, including rates of several representative systems. Particular details of each system are given in the following.

Table I. Summary of Observed Reactions

Reaction	ΔH, kcal/mol[a]	Rate[b]
$(CH_3)_3CH + NO^+ \rightarrow (CH_3)_3C^+ + HNO$	−2	8.1
$CH_3CHO + NO^+ \rightarrow CH_3CO^+ + HNO$	−4	3.5
$CH_3CH_2OH + NO^+ \rightarrow CH_3CHOH^+ + HNO$		8.0
$(CH_3)_2CHOH + NO^+ \rightarrow (CH_3)_2COH^+ + HNO$	−19	
$(CH_3)_3COH + NO^+ \rightarrow (CH_3)_3C^+ + HONO$	−10	19
$CH_3CHOHCH_2CH_2CH_3 + NO^+ \rightarrow CH_3COHCH_2CH_2CH_3^+ + HNO$	−22	
$\rightarrow CH_3CHCH_2CH_2CH_3^+ + HONO$	−5	
$(CH_3)_3Cl + NO^+ \rightarrow (CH_3)_3C^+ + ClNO$	−9	
$(CH_3)_2CHCl + NO^+ \rightarrow (CH_3)_2CH^+ + ClNO$	+3	
$\rightarrow (C_3H_6)NO^+ + HCl$		4.6[c,d]
$(C_3H_6)NO^+ + (CH_3)_2CHCl \rightarrow [(CH_3)_2CHCl]NO^+ + C_3H_6$		
$C_6H_5CH_2F + NO^+ \rightarrow C_7H_7^+ + FNO$	−7	
$(CH_3)_2CHF + NO^+ \rightarrow HFNO^+ + C_3H_6$		
$\rightarrow (C_3H_6)NO^+ + HF$		4.6[c]
$HFNO^+ + (CH_3)_2CHF \rightarrow [(CH_3)_2CHF]NO^+ + HF$		10.4
$(C_3H_6)NO^+ + (CH_3)_2CHF \rightarrow [(CH_3)_2CHF]NO^+ + C_3H_6$		

[a] Values are calculated from data in Tables II and III. [b] Units of 10^{-10} cm^3 molecule^{-1} sec^{-1}. [c] There are indications that the kinetics of the individual reactions may depend on the internal energy state of the NO^+ parent. Only an overall rate for the disappearance of NO^+ at long times is given. [d] For $(CD_3)_2CHCl$, the disappearance rate of NO^+ is 2.4×10^{-10} cm^3 molecule^{-1} sec^{-1}

Isobutane. Isobutane was studied for comparison with the results of Searles and Sieck.[11] Only the hydride transfer reaction 1 is observed, in agreement with their work. Our

$$NO^+ + (CH_3)_3CH \longrightarrow (CH_3)_3C^+ + HNO \qquad (1)$$

measured rate of 8.1×10^{-10} cm^3 molecule^{-1} sec^{-1} does not compare well with their value of 4.6×10^{-10} cm^3 molecule^{-1} sec^{-1}. This discrepancy may be due to the indirect method of determining rate constants used by Searles and Sieck.[11]

Acetaldehyde. NO^+ reacts with acetaldehyde in accordance with the hydride transfer reaction 2. The acetyl cat-

$$NO^+ + CH_3CHO \longrightarrow CH_3CO^+ + HNO \qquad (2)$$

ion thus formed does not react further with either neutral species.

Ethanol, 2-Propanol, *tert*-Butanol, and 2-Pentanol. With aliphatic alcohols hydride or hydroxide transfer can occur, as indicated in reactions 3-7. Figure 1 shows the variation

$$CH_3CH_2OH + NO^+ \longrightarrow CH_3CHOH^+ + HNO \qquad (3)$$

$$(CH_3)_2CHOH + NO^+ \longrightarrow (CH_3)_2COH^+ + HNO \qquad (4)$$

$$(CH_3)_3COH + NO^+ \longrightarrow (CH_3)_3C^+ + HONO \qquad (5)$$

$$CH_3CHOHCH_2CH_2CH_3 + NO^+ \longrightarrow CH_3COHCH_2CH_2CH_3^+ + HNO \qquad (6)$$

$$ \longrightarrow CH_3CHCH_2CH_2CH_3^+ + HONO \qquad (7)$$

of ion abundance with time in a mixture of NO and ethanol. An ion of formula $C_2H_5O^+$ is produced by NO^+ in this system. Use of C_2D_5OH shows that the hydride transfer occurs exclusively from the alkyl function. Thermodynamic considerations strongly favor the methylene group as the reactive site.[26] Like ethanol, 2-propanol reacts only by α-hydride transfer. With *tert*-butyl alcohol, which has no α hydrogen, only hydroxide transfer is observed. 2-Pentanol exhibits both hydride and hydroxide transfer, the rate of hydride transfer being 16 times the rate of hydroxide transfer. No evidence of other reactions due to NO^+ was found with any of the alcohols. In all four systems, further reactions of the product ions occur along with reactions of the primary ions of the alcohols. These reaction sequences have been previously described in detail.[22-24]

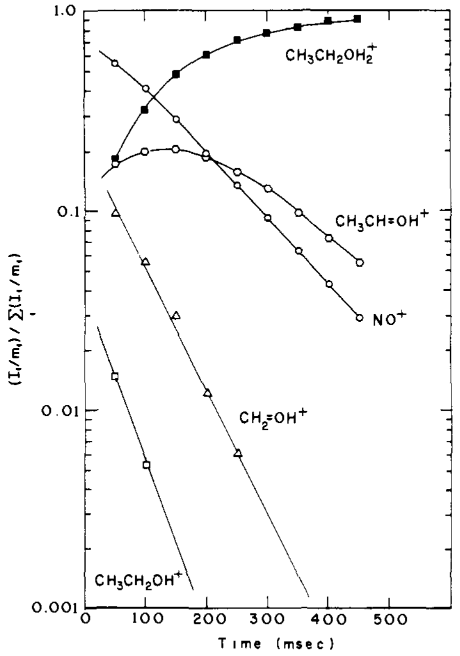


Figure 1. Variation of ion abundance with time for a mixture of 2.59×10^{-7} Torr of ethanol and 9.88×10^{-7} Torr of nitric oxide ionized at 14.0 eV. Ionization was initiated by an 11 msec electron beam pulse.

Hunt and Ryan[10] report observation of M − 1 (hydride transfer) and M − 17 (hydroxide transfer) ions in NO^+ chemical ionization of alcohols in agreement with the results of this work. However, their study also reports ions corresponding to M − 2 + 30 with primary and secondary alcohols and M − 3 with primary alcohols. These products were not observed in our study. As suggested by Hunt and Ryan,[10] it is possible that these ions result from oxidation of the neutral alcohol followed by reaction of NO^+ with the resulting aldehyde or ketone.

***tert*-Butyl Chloride and Isopropyl Chloride.** With *tert*-butyl chloride, NO^+ reacts exclusively by chloride transfer (reaction 8). In isopropyl chloride, reaction 9 is observed in

$$(CH_3)_3CCl + NO^+ \longrightarrow (CH_3)_3C^+ + ClNO \qquad (8)$$

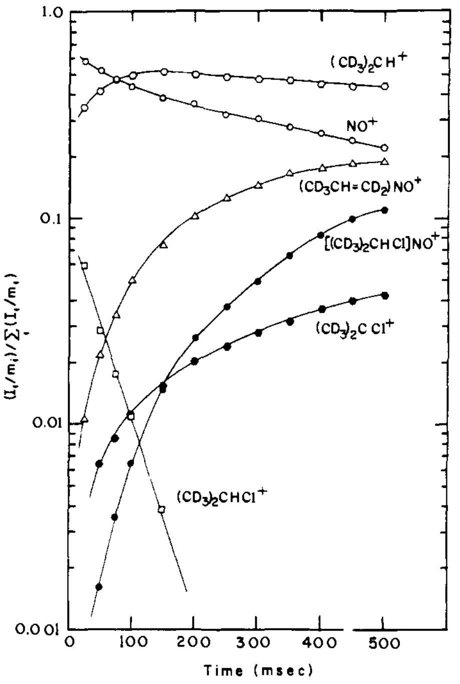


Figure 2. Variation of ion abundance with time in a mixture of 2.04 × 10^{-7} Torr of $(CD_3)_2CHCl$ and 9.9 × 10^{-7} Torr of NO at 13.5 eV. Ionization was initiated by an 11 msec electron beam pulse.

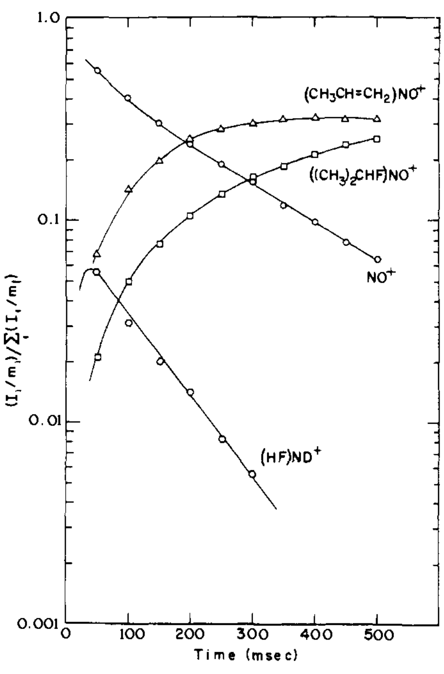


Figure 3. Variation of ion abundance with time of a mixture of 2.19 × 10^{-7} Torr of isopropyl fluoride and 6.56 × 10^{-7} Torr of nitric oxide at 14.0 eV. Ionization was initiated by an 11 msec electron beam pulse. Not displayed are ions at *m/e* 43, 47, 61, and 85, due to reactions of primary ions of isopropyl fluoride with the parent neutral.

addition to the chloride transfer reaction 10. The product ions of both reactions 9 and 10 react further with isopropyl

$$(CH_3)_2CHCl + NO^+ \begin{cases} \longrightarrow (C_3H_6)NO^+ + HCl & (9) \\ \longrightarrow (CH_3)_2CH^+ + ClNO & (10) \end{cases}$$

chloride according to reactions 11 and 12, respectively.

$$(C_3H_6)NO^+ + (CH_3)_2CHCl \longrightarrow [(CH_3)_2CHCl]NO^+ + C_3H_6 \quad (11)$$

$$(CH_3)_2CH^+ + (CH_3)_2CHCl \longrightarrow (CH_3)_2CCl^+ + C_3H_8 \quad (12)$$

Reaction 12 involves hydride transfer, while reaction 11 appears to involve transfer of NO^+ from the product of reaction 9 to isopropyl chloride.

In order to illucidate the nature of the reaction sequence 9 and 11, the isotopically labeled species $(CD_3)_2CHCl$ was examined. As shown in Figure 2, the deuterated chloride reacts with the label retention indicated in reactions 13 and 14. The reaction intermediate in process 13 undergoes a 1,2

$$(CD_3)_2CHCl + NO^+ \longrightarrow (CD_3CHCD_2)NO^+ + DCl \quad (13)$$

$$(CD_3CHCD_2)NO^+ + (CD_3)_2CHCl \longrightarrow [(CD_3)_2CHCl]NO^+ + CD_3CHCD_2 \quad (14)$$

loss of DCl to form what appears to be a complex of NO· with propylene.

The data in Figure 2 suggest that excited states of NO^+ may be involved in reaction 10. The sum of the signals $(CH_3)_2CH^+$ and $(CH_3)_2CCl^+$ [due to reactions 10 and 12] builds up rapidly to a constant level while the loss of NO^+ at longer times seems to be accounted for only by the continual increase in the products of reactions 9 and 11. Furthermore, the curvature of the decay of NO^+ is consistent with the participation of excited states in the overall scheme of reactions.

If π-donor bases (B) such as benzene or *cis*-2-butene are added to a reaction mixture of NO and isopropyl chloride,

$$(CH_3CHCH_2)NO^+ + B \longrightarrow BNO^+ + CH_3CH{=}CH_2 \quad (15)$$

$$[(CH_3)_2CHCl]NO^+ + B \longrightarrow BNO^+ + (CH_3)_2CHCl \quad (16)$$

NO^+ transfer reactions 15 and 16 are observed. These findings are consistent with a loosely bound π complex as the ionic product of reaction 9.

Benzyl Fluoride, Isopropyl Fluoride, and 2,2-Difluoropropane. Benzyl fluoride reacts with NO^+ exclusively by the fluoride transfer reaction 17. Unlike benzyl fluoride, isopropyl fluoride does not react with NO^+ by fluoride transfer.

$$C_6H_5CH_2F + NO^+ \longrightarrow C_7H_7^+ + FNO \quad (17)$$

With isopropyl fluoride the reaction sequences 18-21 are

$$(CH_3)_2CHF + NO^+ \longrightarrow (C_3H_6)NO^+ + HF \quad (18)$$

$$(C_3H_6)NO^+ + (CH_3)_2CHF \longrightarrow [(CH_3)_2CHF]NO^+ + C_3H_6 \quad (19)$$

$$(CH_3)_2CHF + NO^+ \longrightarrow HFNO^+ + C_3H_6 \quad (20)$$

$$HFNO^+ + (CH_3)_2CHF \longrightarrow [(CH_3)_2CHF]NO^+ + HF \quad (21)$$

observed. Reactions 18 and 19 are analogous to reactions 9 and 11 of isopropyl chloride. HF is eliminated from the fluoride, with NO^+ remaining bound to propylene. This complex then transfers NO^+ to isopropyl fluoride. Reactions 20 and 21 constitute an alternate pathway to the $[(CH_3)_2CHF]NO^+$ terminal ion. In this sequence HF elimination from isopropyl fluoride also occurs, but NO^+ remains bound to HF rather than propylene. The resulting $HFNO^+$ ion transfers NO^+ to isopropyl fluoride (reaction 21). Figure 3 illustrates the variation of ion abundance with time in the nitric oxide-isopropyl fluoride system.

As was the case for reaction 10 of isopropyl chloride, there are indications in Figure 3 that reaction 20 proceeds rapidly with NO^+ with excess internal energy and slowly, if at all, with ground state NO^+. On the time scale shown in Figure 3, the product $HFNO^+$ rises almost immediately to a maximum and decays rapidly (with a rate of 1.04 × 10^{-9}

Table II. Thermochemical Data[a]

Compd	$\Delta H_f{}^\circ{}_{298}$	Compd	$\Delta H_f{}^\circ{}_{298}$
NO	21.57[b]	HONO	−18.58[i]
CH_3F	−55.9[c]	ClNO	12.57[j]
C_2H_5F	−62.5[d]	FNO	−15.8[k]
$(CH_3)_2CHF$	−69.0[e]	H^-	33.39[b]
$(CH_3)_3CF$	−74.1[f]	OH^-	−33.67[b]
$C_6H_5CH_2F$	−29.7[g]	Cl^-	−55.9[l]
HNO	31.7[h]	F^-	−61.3[m]

[a] Data given only for particularly relevant species. All other thermochemical data used in constructing Table III are from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970. [b] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 26 (1969). [c] J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3**, 427 (1971). [d] J. R. Lacher and H. A. Skinner, *J. Chem. Soc.*, 1034 (1968). [e] J. R. Lacher, *J. Phys. Chem.*, 60, 1454 (1956). [f] Estimated using group equivalent methods of Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968. [g] Estimated from methods of substitution constants in "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969. [h] J. L. Holmes, *Proc. Chem. Soc., London*, **75** (1962). [i] P. G. Ashmore and B. J. Tyler, *J. Chem. Soc.*, 1017 (1961). [j] C. M. Beeson and D. M. Yost, *J. Chem. Phys.*, 7, 44 (1939). [k] H. S. Johnston and H. J. Bertin, *J. Am. Chem. Soc.*, 81, 6402 (1959). [l] *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37, 1971. [m] W. A. Chypka and J. Berkowitz, *J. Chem. Phys.* **54**, 5126 (1971); J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, *J. Chem. Phys.*, **54**, 5165 (1971).

cm^3 $molecule^{-1}$ sec^{-1}) while the concentration of NO^+ is still appreciable. Reactions 18 and 19 are slower; however, double resonance studies show that at long times this sequence accounts for 85% of the reacted NO^+.

2,2-Difluoropropane was investigated with the expectation that condensation or elimination reactions would be observed, but no reactions of this species with NO^+ were detected.

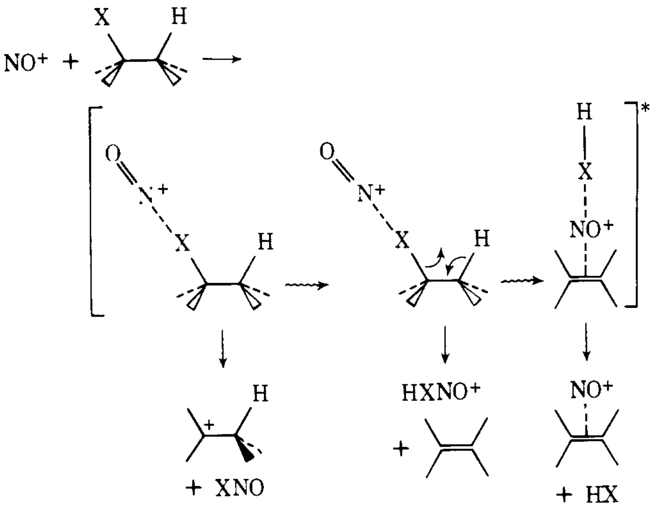
Discussion

Classification of Observed Reactions. Recent experiments in our laboratories[21,29] have demonstrated that halide transfer reactions between carbonium ions (eq 22) are rapid and can be employed to determine R^+-X^- heterolytic bond

$$R_1^+ + R_2X \rightleftharpoons [R_1XR_2^+]^* \rightleftharpoons R_1X + R_2 \tag{22}$$

energies $D(R^+\text{-}X^-)$. Using available thermochemical data (summarized in Table II), a comparison of ON^+-X^- heterolytic bond energies for the appropriate nitrosyl compounds to $D(R^+\text{-}X^-)$ for various carbonium ions can be made (Table III). The data in Table III indicate the following order of decreasing bond strengths for $X^- = Cl^-$: $CH_3^+ > C_2H_5^+ > (CH_3)_2CH^+ > NO^+ > CH_3CO^+ > (CH_3)_3C^+ > C_6H_5CH_2^+$. The order is slightly different for other anions (Table III). This predicted order is consistent with our observations in all cases except reaction 10, which is suspected to involve vibrationally excited NO^+. Since anion transfer is observed to occur wherever possible according to the relative heterolytic bond energies, these considerations may be useful in predicting anion transfer reactions to NO^+ with other compounds.

Scheme I



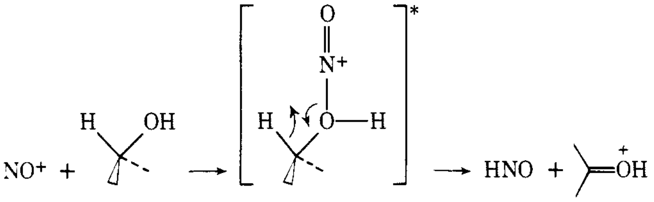
The reactions of NO^+ observed in this and previous studies can be classified as anion transfer or, in the case of alkyl halides (RX) possessing β hydrogen, as elimination reactions with NO^+ remaining bound to either HX or to the resulting alkene. These processes can be discussed in terms of the general reaction Scheme I. As illustrated in Scheme I, NO^+ is envisioned to act as a Lewis acid, binding to the n-donor base site in the reactant neutral and forming a chemically activated intermediate. The most commonly observed process involves decomposition of the reaction intermediate to yield XNO and the corresponding carbonium ion (anion transfer). Anion transfer involves a simple bond cleavage in the intermediate in Scheme I and should have a high frequency factor. The elimination processes are most prevalent when the facile anion transfer reaction is endothermic [e.g., with isopropyl fluoride (reactions 18 and 20)]. The direct elimination to yield $HXNO^+$ bears an interesting analogy to the dehydration reactions effected by the interaction of Brønsted acids with aliphatic alcohols.[26-28,30] The remaining elimination, in which HX is lost and NO^+ forms a π complex with the alkene, appears to involve further rearrangement of the reaction intermediate indicated in Scheme I. The factors that determine which of the two elimination

Table III. Heterolytic Bond Dissociation Energies

R^+	$\Delta H_f{}^\circ{}_{298}(R^+)$	$D(R^+\text{–}H^-)$	$D(R^+\text{–}OH^-)$	$D(R^+\text{–}Cl^-)$	$D(R^+\text{–}F^-)$
NO^+	239.9[a]	237	219.8	166.4	189.4
CH_3^+	260.9[b]	312.2	275.3	225.6	255.9
$CH_3CH_2^+$	219.0[b]	272.6	241.6	189.2	220.3
$(CH_3)_2CH^+$	191.7[b]	249.9	223.2	169.4	199.4
CH_3CO^+	160[c]	233.1	229.6	162	204
$(CH_3)_3C^+$	169.1[b,d]	234.9	210.2	156.9	182
$C_6H_5CH_2^+$	213[e]	234.1	203.2	153	182
$CH_3CHCH_2CH_2CH_3^+$	173[a]	241	215		
CH_3CHOH^+	141.4[f]	231.2[f]			
$(CH_3)_2COH^+$	119[g]	218			
$CH_3COHCH_2CH_2CH_3^+$	107[h]	215			

[a] Reference *a*, Table II. [b] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 48, 955 (1970). [c] D. Reinke, R. Krässig, and H. Baumgärtel, *Z. Naturforsch., Teil A*, 28, 1021 (1973). [d] W. Tsang, *J. Phys. Chem.*, 76, 143 (1972). [e] F. P. Lossing, *Can. J. Chem.*, 49, 357 (1971). [f] K. M. A. Rafaey and W. A. Chupka, *J. Chem. Phys.*. 48, 5205 (1968). [g] S. E. Buttrill and J. L. Beauchamp, unpublished photoionization studies. [h] Group additivity estimate.

Scheme II



products predominates are not clear. The relative base strengths of HX and the alkene toward NO^+ are likely to be important, since this affects the relative exothermicity of the two elimination pathways.

The rapid transfer of NO^+ between various π- and n-donor bases suggests that the ionic species involved are loosely bound complexes. Equilibrium studies of these reactions are currently under investigation in our laboratories to determine accurate relative NO^+ binding energies. The binding energy of NO^+ to H_2O is known,[3e] providing a means of determining an absolute scale of binding energies of NO^+ to various bases.

Reactions of NO^+ with alcohols cannot be classified according to Scheme I. While anion transfer occurs in accordance with the relative heterolytic bond dissociation energies, the elimination reactions of Scheme I are not observed. Instead, the typical reaction pathway involves the postulated four-center elimination of HNO from the activated complex shown in Scheme II. The overall process thus involves α-hydride transfer. From our results we may hypothesize a general pattern for reaction of NO^+ with alcohols. We propose that tertiary alcohols react exclusively by OH^- transfer, and that primary alcohols exhibit only α-hydride transfer. Higher secondary alcohols react in both ways, with the hydride transfer predominant.

Lewis Acid Character of NO^+. Recent studies in our laboratory[32] have revealed several new reactions of alkali ions, particularly Li^+. It is observed that Li^+ ions undergo all the reactions in Scheme I, as well as Li^+ transfer between both π- and n-donor bases. Since alkali ions have the electronic structure of rare gases, their gas phase reactivity is best ascribed to their Lewis acidity. In view of the completely analogous behavior of NO^+ and the alkali ions, it appears that the most important factor in the ion chemistry of NO^+ is its Lewis acid character.

Implications for Radiation Chemistry. It is clear that reactions of NO^+ may play an important role in the overall chemistry of radiolysis studies in which NO is added as a scavenger or inhibitor. It would be of interest to carry out radiolysis experiments in which an excess of NO is used to examine the possibility that some of the ion-molecule reactions newly characterized in this study occur under radiolytic conditions.

Acknowledgment. This research was supported in part by the Energy Research and Development Administration under Grant No. AT(05-3)767-8. The instrument used for these studies was funded by the National Science Foundation under Grant No. NSF-GP-18383.

References and Notes

(1) Dreyfus Teacher-Scholar, 1971–1976.

(2) (a) W. C. Lineberger, and L. J. Puckett, *Phys. Rev.*, **186**, 116 (1969); (b) L. J. Puckett and M. W. Teague, *J. Chem. Phys.*, **54**, 2564 (1971).

(3) (a) W. C. Lineberger and L. J. Puckett, *Phys. Rev.*, **187**, 286 (1969); (b) F. C. Fehsenfeld, M. Mosesman, and E. E. Ferguson, *J. Chem. Phys.*, **55**, 2120 (1971); (c) C. J. Howard, H. W. Rundle, and F. Kaufman, *ibid.*, **55**, 4772 (1971); (d) M. J. McAdams and L. I. Bone, *ibid.*, **57**, 2173 (1972); (e) M. A. French, L. P. Hills, and P. Kebarle, *Can. J. Chem.*, **51**, 456 (1973).

(4) L. J. Puckett and M. W. Teague, *Trans. Am. Geophys. Union*, 366 (1970).

(5) D. B. Dunkin, F. C. Fehsenfeld, A. L. Schmeltekopf, and E. E. Ferguson, *J. Chem. Phys.*, **54**, 3817 (1971).

(6) F. C. Fehsenfeld, *J. Chem. Phys.*, **61**, 1588 (1974). The same author reports a bimolecular sequence with rate less than 10^{-14} cm^3 mol^{-1} sec^{-1} in *J. Geophys. Res.*, **78**, 327 (1973).

(7) D. L. Turner and L. I. Bone, *J. Phys. Chem.*, **78**, 501 (1974).

(8) W. Shultz, H. Drost, and H.-D. Klotz, *Org. Mass Spectrom.*, **1**, 391 (1968).

(9) N. Einolf and B. Munson, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 141 (1972).

(10) D. F. Hunt and J. F. Ryan, *Chem. Commun.*, 620 (1972).

(11) S. K. Searles and L. W. Sieck, *J. Chem. Phys.*, **53**, 794 (1970).

(12) For a discussion of the use of NO as a free radical scavenger, see E. W. R. Steacie, "Atomic and Free Radical Reactions", Reinhold, New York, N.Y., 1954, pp 56 and 109–124, and references therein.

(13) For example, see G. G. Meisels, *J. Chem. Phys.*, **42**, 3237 (1965).

(14) P. R. LeBreton, A. D. Williamson, J. L. Beauchamp, and W. T. Huntress, *J. Chem. Phys.*, **62**, 1623 (1975).

(15) P. C. Killgoar, C. E. Leroi, J. Berkowitz, and W. A. Chupka, *J. Chem. Phys.*, **58**, 803 (1973), and references therein.

(16) K. Tanaka, K. Honma, I. Koyano, and I. Tanaka, *J. Chem. Phys.*, **60**, 3347 (1974).

(17) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, London, 1970, pp 37–39.

(18) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(19) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

(20) M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 4815 (1975).

(21) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1269 (1974).

(22) T. B. McMahon, Ph.D. Thesis, California Institute of Technology, 1973.

(23) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **74**, 5285 (1952).

(24) J. F. Norris and H. B. Taylor, *J. Am. Chem. Soc.*, **46**, 753 (1924).

(25) (a) A. S. Blair and A. G. Harrison, *Can. J. Chem.*, **51**, 703 (1973); (b) H. Pritchard and A. G. Harrison, *J. Chem. Phys.*, **48**, 5623 (1968).

(26) For a discussion of the relative stabilities of various $C_2H_5O^+$ isomers, see J. L. Beauchamp and R. C. Dunbar, *J. Am. Chem. Soc.*, **92**, 1477 (1970).

(27) (a) L. W. Sieck, F. P. Abramson, and J. H. Futrell, *J. Chem. Phys.*, **45**, 2859 (1966); (b) K. R. Ryan, L. W. Sieck, and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

(28) J. L. Beauchamp, M. C. Caserio, and T. B. McMahon, *J. Am. Chem. Soc.*, **96**, 6243 (1974).

(29) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **94**, 8934 (1972).

(30) J. L. Beauchamp, *J. Am. Chem. Soc.*, **91**, 5925 (1969).

(31) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 924 (1975).