values equals

$$\ln A_{\text{obsd}} - \ln(\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}) + (n - 1)\ln A_f^0$$

where n is the number of points in the set, and the sum of the abscissa values equals

$$\ln(k_{\text{H}}/k_{\text{D}})_{\text{obsd}} - \ln(\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}) + (n - 1)\ln(f^0 \text{ ratio})$$

The composite model constructed by combining the transition-state force constants corresponding to the chosen points should simultaneously reproduce the observed kie at the reference temperature and the observed Arrhenius preexponential factor. Small adjustments can be made on the final model in order to make the fit more exact.

When only two kinds of force-constant changes are permitted in the composite model, those force-constant changes are uniquely determined (aside from the final adjustments) by the necessity of fitting both the observed kie and A factor.[22] For reactions where preliminary mechanistic considerations allow n possible kinds of force-constant changes at the isotopic position(s), $n - 2$ must be fixed before the remaining two can be determined. Thus, the proposed systematic method of force-field fitting, although much less arbitrary than trial and error methods, does not necessarily uniquely determine the transition-state force field. However, it does limit the possibilities to which final mechanistic considerations must be applied. Usually, other mechanistic considerations allow one to fix a range for at least one type of force-constant change. Then graphs such as Figure 4 enable one at least to bracket the changes in the other force constants.[23]

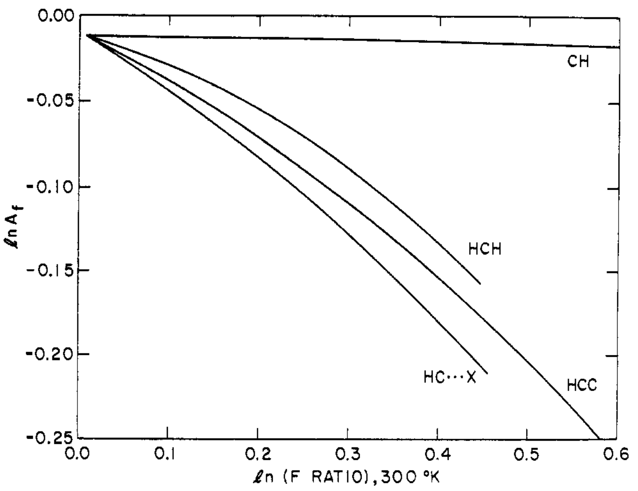

Figure 4. Plot of Arrhenius intercept *vs.* quantum kinetic isotope effect for α-D_2 SN1 models.

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[22] For certain unusual and fortuitous combinations of curves and observed values, the determination of the two points may not be unique.

[23] The fairly close transferability of the slopes of plots of $\ln A_f$ *vs.* $\ln$ (f ratio) among the different model reaction types prompted us to attempt the development of a simple method of using experimental Arrhenius preexponential factors to gain limited mechanistic information without carrying out detailed model calculations. Our efforts resulted in a method which provided reliable information as to the relative magnitudes of the stretching and bending force-constant change contributions to an isotope effect *only* if f^0 ratio, A_f^0, and $\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}$ were known accurately. As f^0 ratio and A_f^0 are strictly theoretical quantities and there is, at present, no way to extract $\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}$ from experimental data in the room-temperature region, we do not feel that the method warrants further exploration.

Ion–Molecule Reactions and the Proton Affinities of the Nitroalkanes. I. Nitromethane and Nitroethane

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Abstract: Ion cyclotron single and double resonance techniques have been used to study the positive ion–molecule chemistry of nitromethane and nitroethane. The reactions in nitromethane can be divided into four classes: (1) proton transfer to nitromethane; (2) methyl cation transfer from CH_3NO^+ and $CH_3NO_2^+$ to nitromethane; (3) NO^+ transfer from $CH_2NO_2^+$; and (4) an unusual O^- abstraction by methyl cation. The reactions in nitroethane are (1) proton transfer to nitroethane from $C_2H_3^+$, H_3CN^+, and $C_2H_5^+$; (2) NO^+ transfer from $H_2NO_2^+$; and (3) a probable dissociation of protonated nitroethane into $H_2NO_2^+$ and C_2H_4. Deuterium and nitrogen-15 isotopic labeling were used to obtain information on the mechanisms of the reactions. Proton transfer reactions were used to determine that the proton affinity of nitromethane is 180 ± 4 kcal/mol while that of nitroethane is 185 ± 4 kcal/mol. These values correspond to $\Delta H_f(CH_3NO_2H^+) = 168$ and $\Delta H_f(C_2H_5NO_2H^+) = 157$ kcal/mol.

The mass spectra of the nitroalkanes are unusual in that the major peaks are hydrocarbon ions. Only the nitromethane ion is stable with respect to decomposition into an alkyl cation and nitrogen dioxide; no significant molecular ion peaks are observed for any other nitroalkane.[2] This behavior can be understood by considering the electronic structures of the nitroalkanes and their molecular ions. The nitrogen atom in the neutral I already has a formal positive

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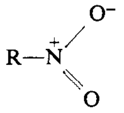
[1] (a) Varian Postdoctoral Fellow, 1968–1969. Ciba-Geigy AG, Department of Physics, CH-4002 Basel, Switzerland. (b) University of Minnesota.

[2] R. T. Alpin, M. Fischer, D. Becher, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 87, 4888 (1965).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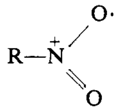
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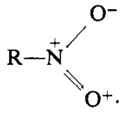
III

charge and four covalent bonds. In other organic compounds, the most common modes of positive ion fragmentation are those in which an odd-electron neutral is lost and the heteroatom which carries the charge forms an additional covalent bond. These processes are favored because (A) reestablishing the octet for the charged atom moves electrons toward the charge and thus stabilizes it, and (B) a new bond is formed, compensating for the one broken in the fragmentation.

The nitroalkane ions (II and III) have the charge localized on nitrogen, but formally the electron has been removed from the oxygens. Formation of an additional bond to nitrogen is impossible; hence there is no particular reason for the charge to be retained in the fragment containing the nitro group. Examination of the energetics of the nitroalkane molecular ion fragmentations reveals that $CH_3\cdot$ is the only alkyl radical with an ionization potential greater than that of NO_2 and that only nitromethane ion is stable with respect to decomposition into an alkyl cation and NO_2.[3]

One of the reasons that conventional mass spectra are useful in identifying compounds is the fact that the functional group apparently directs the ionic fragmentation processes; that is, the major modes of fragmentation are common to the entire class of compounds.[4] The functional group seems to be equally important in ion-molecule chemistry. Most reactions are essentially reactions of or at the functional group. Benezra and Bursey recently reported a reaction of substituted phenols in which reaction was inhibited when the phenol group was sterically blocked.[5] In view of the importance of the functional group in ion-molecule chemistry and the unusual charge destabilizing character of the nitro group, we have used ion cyclotron resonance (icr) techniques to study the ion-molecule chemistry of nitroalkanes.

Results and Discussion

Nitromethane. The relative intensities of the peaks in the icr spectra of nitromethane at 2×10^{-7} and 10^{-5} Torr are given in Table I. Where more than one ionic species is listed with the same value of *m*/*e*, they have all been detected at low pressure in a conventional high resolution mass spectrometer.[6]

Table I. Icr Spectra of Nitromethane at Low and High Pressure (50 eV)

		Relative intensities, %	
m/*e*	Species	2×10^{-7} Torr	10^{-5} Torr
15	CH_3^+	9.7	10.8
27	$CHN\cdot^+$	3.5	6.9
28	$N_2\cdot^+$, $CO\cdot^+$, CH_2N^+	30.0	49.7
29	CHO^+, $CH_3N\cdot^+$	3.9	7.6
30	NO^+, $CH_2O\cdot^+$	62.4	100.8
42	CNO^+	0.5	1.3
43	$CHNO\cdot^+$	2.9	2.3
44	CH_2NO^+, $CO_2\cdot^+$	16.4	18.4
45	$CH_3NO\cdot^+$	7.2	28.8
46	NO_2^+	46.8	83.1
60	$CH_2NO_2^+$	8.5	6.9
61	$CH_3NO_2\cdot^+$	100.0	100.0
62	$CH_3NO_2H^+$	2.8	34.8
76	$CH_3NO_2CH_3^+$		51.5
91	$CH_3N_2O_3^+$		7.8

Table II. Nitromethane Ion–Molecule Reactions[a]

Reaction	ΔH^b
(1) $HCN\cdot^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + CH$	−65
(2) $CH_2N^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + HCN$	−10
(3) $CHO^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + CO$	−36[c]
(4) $CHNO\cdot^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + CNO\cdot$	−21[d,e]
(5) $CH_2NO^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + CHNO$	≤0
(6) $CH_3NO\cdot^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + \cdot CH_2NO$	≤0
(7) $CH_3^+ + CH_3NO_2 \rightarrow CH_3NO\cdot^+ + CH_3O\cdot$	−55[f]
(8) $CH_3NO\cdot^+ + CH_3NO_2 \rightarrow C_2H_6NO_2^+ + \cdot NO$	≤0
(9) $CH_3NO_2\cdot^+ + CH_3NO_2 \rightarrow C_2H_6NO_2^+ + \cdot NO_2$	≤0
(10) $CH_2NO_2^+ + CH_3NO_2 \rightarrow CH_3N_2O_3^+ + CH_2O$	≤0

[a] All had negative double resonance signals. [b] Values in kcal/mol. Taken from ref 3 and 15 except as noted. [c] PA(CO) = 144 kcal/mol: C. S. Matthews and P. Warneck, *J. Chem. Phys.*, **51**, 854 (1969). [d] H. Okabe, *ibid.*, **53**, 3507 (1970). [e] C. G. Rowland, J. H. D. Eland, and C. J. Danby, *Chem. Commun.*, 1535 (1968). [f] Reference 12.

The positive ion-molecule reactions in pure nitromethane which have been verified by double resonance experiments[7] in both nitromethane and nitromethane-d_3 are summarized in Table II together with the sign of the double resonance signal. The double resonance signal is proportional to dk/dE_{ion} in the limit of small irradiating field amplitudes[8] which increase the reactant ions' average energy without changing their concentration within the icr cell. Larger irradiating fields may actually eject reactant ions, but the observation of a negative double resonance signal still implies that the indicated reaction was occurring in the absence of the double resonance irradiation.

Reactions 1–6 are exothermic proton transfer reactions and all are consistent with the proton affinity of nitromethane (see below). The reaction of methyl cation with nitromethane (reaction 7) produces CH_3NO^+ (*m*/*e* 45) and presumably a methoxide radical. The double resonance spectra of *m*/*e* 45 and 48 in a mixture of nitromethane-d_3 and nitromethane indicated that all three hydrogens in the methyl cation are incorporated into the neutral product. This observation rules out attack at the nitrogen since the resulting reaction complex[9] would have equivalent methyl groups. It is difficult to imagine a mechanism for this reaction ini-

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[3] (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. (b) The ionization potential of NO_2 is uncertain, but recent photoionization results set an upper limit of 9.62 eV: P. C. Killgoar, Jr., G. E. Leroi, J. Berkowitz, and W. Chupka, paper presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

[4] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

[5] S. A. Berezra and M. M. Bursey, *J. Amer. Chem. Soc.*, **94**, 1024 (1972).

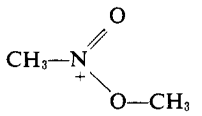
[6] J. Diekman, private communication.

[7] For descriptions of this technique see (a) P. Kriemler and S. E. Buttrill, Jr., *J. Amer. Chem. Soc.*, **92**, 1123 (1970); (b) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

[8] J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

[9] By reaction complex we mean the excited intermediate which fragments to form the ion-molecule reaction products. It corresponds to a minimum in the potential surface for the reaction; see S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 6174 (1970).

tiated by attack at the nitromethane carbon; hence the CH_3^+ ion must react at oxygen. The reaction complex presumably has the structure IV. In addition to

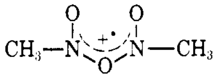


IV

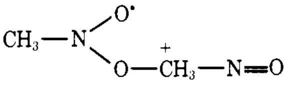
the isotopic labeling results this structure is favored for two reasons: (A) the long-range ion-dipole interaction should bring the positive ion and the negative oxygen together during the collision;[10] and (B) IV is the only reaction complex which allows all atoms to achieve maximum covalency without extensive rearrangement. Homolytic cleavage of the N-OCH_3 bond in IV leads to the observed $CH_3NO\cdot^+$ product.

Reaction 7 is very unusual in that two radical species are produced from two even-electron species. This type of reaction is not normally observed because the higher heats of formation of odd-electron species make them energetically unfavorable or impossible. The methyl cation is such an energetic species however that reaction 7 is exothermic by 55 kcal/mol.

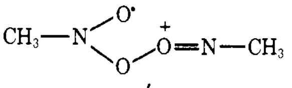
Reactions 8 and 9 are especially interesting since the product ion in both cases is presumably IV. Both formally correspond to a methyl cation transfer. Double resonance studies on nitromethane containing 60% nitrogen-15 showed that in reaction 8 the nitrogen in the product ion came exclusively from the neutral reactant whereas in reaction 9 it came with equal probability from either the ionic or neutral reactant. This result rules out the chemically reasonable but symmetrical structure V as the reaction complex for reaction 8. The other two possible structures for the reaction complex of reaction 8 are VI and VI′, but there is no isotopic labeling experiment which can distinguish between them. If VI is the reaction complex, then the fragmentation to products is a simple C–NO bond cleavage. If VI′ is correct, then the methyl group must be transfered to the oxygen radical site prior to or simultaneously with cleavage of the O–ON bond. The double resonance results for reaction 9 favor a reaction complex structure analogous to VI′ in which both nitrogens would be equivalent. However, the same result would be obtained if the distinction between ionic and neutral reactant is destroyed by rapid, resonant charge transfer reactions as the complex forms. Thus a definite conclusion is impossible and a structure similar to VI cannot be ruled out for the reaction complex of reaction 9.



V



VI



VI′

Holtz, *et al.*,[11] have reported a number of ion–molecule reactions which have the character of nucleophilic displacement reactions (an even-electron neutral with a nonbonding pair of electrons forms a new bond to a carbon atom in an even electron cation displacing an even-electron neutral). They define the methyl cation affinity (MCA) of a species as the negative of the enthalpy change for the process $M + CH_3^+ \rightarrow MCH_3^+$. The methyl cation affinity of the NO_2 radical for N alkylation is 30 kcal/mol[3a] which is substantially less than most of those tabulated by Holtz, *et al.*, for even electron neutrals. On the other hand, the occurrence of reaction 8 implies that $MCA(CH_3NO_2) \geq 99$ kcal/mol ($\Delta H_f(CH_3NO^+) = 183$ kcal/mol[12]). Thus nitromethane should have a rich ion–molecule chemistry; it can undergo reactions in which the weak CH_3^+–NO_2 bond is broken and the neutral molecule can form strong bonds to CH_3^+ and other cations. Reaction 9 is an example of both of these reaction modes. However, care must be exercised in predicting ion–molecule reactions on the basis of thermochemistry alone. For example, the methyl cation affinity of CO is 82 kcal/mol indicating that CH_3CO^+ should transfer a methyl cation to nitromethane; but in a 1:1 mixture of CD_3NO_2 and acetone, this reaction is not observed. Details of the reactions of nitromethane with several other compounds will be reported in future publications.

The minor ion $CH_2NO_2^+$ can transfer NO^+ to nitromethane as shown by reaction 10. Double resonance experiments on a mixture of nitromethane and nitromethane-d_3 showed that the hydrogens in the $CH_3N_2O_3^+$ product ion come exclusively from the neutral reactant. The reactions in a mixture of nitromethane and benzene were studied in an effort to further elucidate the mechanism of reaction 10. Schulz, *et al.*,[13] studied this system and concluded from appearance potential measurements that the reactions

$$CH_3NO_2^+ + CH_3NO_2 \longrightarrow CH_3N^+O_2NO + CH_3O \quad (11)$$

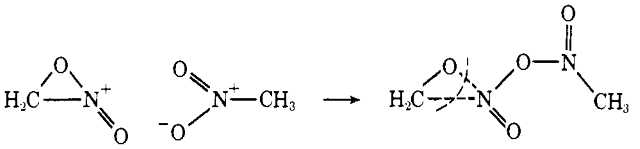
$$CH_3NO_2^+ + C_6H_6 \longrightarrow C_6H_6NO^+ + CH_3O \quad (12)$$

were the sources of the nitrosation products. We can find no hint of a double resonance signal for either reaction 11 or 12, but we do find clear signals indicating the occurrence of reactions 10 and 13. We conclude that

$$CH_2NO_2^+ + C_6H_6 \longrightarrow C_6H_6NO^+ + CH_2O \quad (13)$$

reactions 11 and 12 do not occur, at least under the conditions of this study.

Although the above results characterize reaction 10 as a NO^+ transfer they do not provide enough information to unambiguously identify the reaction mechanism. Even the structure of the $CH_2NO_2^+$ ion is not certain. However, we suggest the following as the most chemically reasonable mechanism consistent with the results.



With our present equipment, it is not possible to perform a double resonance experiment to check for the reaction

$$CH_3NO_2^+ + CH_3NO_2 \longrightarrow CH_3NO_2H^+ + CH_2NO_2$$

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(10) L. J. Leger and G. G. Meisels, *Chem. Phys. Lett.*, 2, 661 (1986).

(11) D. Holtz, J. I. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, 92, 7484 (1970).

(12) R. J. Kandel, *J. Chem. Phys.*, 23, 84 (1955).

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

because of the strong coupling between the double resonance and observing oscillators. The possibility of this reaction was examined by measuring the appearance potentials of CH_3NO^+, $CH_3NO_2^+$, and $CH_3NO_2H^+$. The fact that the appearance potential of protonated nitromethane is nearly 2 eV higher than the appearance potential of $CH_3NO_2^+$ clearly shows that unexcited $CH_3NO_2^+$ does not react with nitromethane to form $CH_3NO_2H^+$.

Nitroethane. The 70-eV icr spectra of nitroethane at 2×10^{-7} and 1×10^{-5} Torr are given in Table III. It is noteworthy that the small molecular ion reported by Aplin, *et al.*,[2] is completely absent in these spectra, indicating that this ion is unstable with respect to decomposition into $C_2H_5^+$ and NO_2. In a conventional mass spectrometer some of the molecular ions are mass analyzed prior to their fragmentation, while on the longer time scale of the icr experiment all of the molecular ions fragment before they can be detected. These observations set limits on the unimolecular rate constant, k, for the fragmentation of $10^7 \geq k \geq 10^4$ sec^{-1}.

Table III. Icr Spectra of Nitroethane at Low and High Pressure (70 eV)

		Relative intensities, %	
m/e	Species	2×10^{-7} Torr	10^{-5} Torr
15	CH_3^+	0.1	0.1
26	$C_2H_2\cdot^+$	8.6	5.3
27	$C_2H_3^+$, $HCN\cdot^+$	70.5	47.2
28	$C_2H_4\cdot^-$, $N_2\cdot^+$	26.3	33.8
29	$C_2H_5^+$	100.0	100.0
30	NO^+	14.9	18.8
40		2.3	3.7
41	$C_2H_3N\cdot^+$	1.3	2.5
42		0.5	2.5
43		0.5	1.0
44		1.8	6.5
45			4.4
46	NO_2^+	3.9	4.8
48	$H_2NO_2^+$		3.8
59	$C_2H_5NO\cdot^+$		3.5
60	$CH_2NO_2^+$	1.0	1.0
75	$C_2H_5NO_2\cdot^+$		
76	$C_2H_5NO_2H^+$	4.0	178.5
105	$C_2H_5N_2O_3^+$		7.1

The reactions occurring in pure nitroethane are summarized in Table IV. In contrast to nitromethane, no alkylation of the neutral takes place. Reactions 14–16 are exothermic proton transfer reactions consistent with the proton affinity of nitroethane (see below). Reaction 17 corresponds to transfer of NO^+ to nitroethane similar to reaction 10. Double resonance experiments in a mixture of nitroethane and nitroethane-d_5 show that the hydrogens in the neutral H_2O product come entirely from the ionic reactant. Furthermore, reaction 19 was found to occur in a 1:1 mixture of nitro-

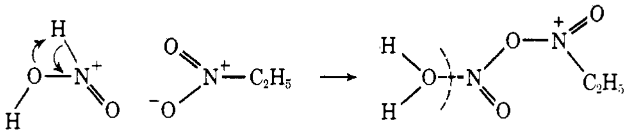
$$H_2NO_2^+ + C_6H_6 \longrightarrow C_6H_6NO^+ + H_2O \qquad (19)$$

ethane and benzene. These results suggest that reaction 17 has the following mechanism similar to that postulated for reaction 10.

Table IV. Nitroethane Ion–Molecule Reactions

Reaction	dk/dE_{ion}	ΔH^a
(14) $C_2H_3^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2H^+ + C_2H_2$	−	−33
(15) $H_2CN^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2H^+ + HCN$	−	−15
(16) $C_2H_5^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2H^+ + C_2H_4$	−	−25
(17) $H_2NO_2^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2NO^+ + H_2O$	−	≤ 0
(18) $C_2H_5NO_2H^+ \rightarrow H_2NO_2^+ + C_2H_4$	+	

[a] Values in kcal/mol from ref 15 and ref 3a.



The origins of the $H_2NO_2^+$ ion (*m/e* 48) itself are somewhat uncertain because of its small relative abundance. Two pieces of evidence suggest that this ion is formed by a dissociative proton transfer to nitroethane. (A) The double resonance spectrum of $H_2NO_2^+$ shows only a small positive peak at *m/e* 76 suggesting the occurrence of reaction 18 (Table IV). This result does *not* prove that reaction 18 occurs in the absence of the double resonance irradiation; it merely shows that a collision induced dissociation[14] corresponding to reaction 18 occurs in the presence of the double resonance irradiation. (B) A 1:1 mixture of nitroethane and nitroethane-d_5 shows single resonance signals at *m/e* 48, 49, and 50 in the ratios 1 : 2 : 1. This result rules out the possibility that the $H_2NO_2^+$ is formed by direct dissociation of a nitroethane molecular ion since the presence of the *m/e* 49 peak requires that the two hydrogens originate from different nitroethane molecules. However, there is no detectable peak in the double resonance spectrum of $H_2NO_2^+$ other than the positive signal from *m/e* 76.

Proton Affinities. The proton affinity (PA) of a molecule, M, is defined as minus the enthalpy change for the reaction $M + H^+ \rightarrow MH^+$. The hydrogen affinity (HA) of an ion is the hydrogen bond strength in the M^+–H ion and is given by

$$HA(M^+) = \Delta H_f(M^+) + \Delta H_f(H) - \Delta H_f(MH^+)$$

As in previous studies,[7a,8] we have placed close limits on the proton affinities of nitromethane and nitroethane by observing reactions of the type

$$M_1H^+ + M_2 \longrightarrow M_2H^+ + M_1 \qquad (20)$$

in which the proton affinity of either the reactant or product neutral is known. Since these reactions are gas-phase bimolecular processes, energy conservation requires that they be exothermic or thermoneutral. Thus the observation of reaction 20 would show that $PA(M_1) \leq PA(M_2)$ and

$$\Delta H = \Delta H_f(M_2H^+) + \Delta H_f(M_1) - \Delta H_f(M_1H^+) - \Delta H_f(M_2) \leq 0$$

The proton transfer reactions observed in nitromethane mixtures are given in Table V together with the limits which they place on $PA(CH_3NO_2)$. All of these reactions showed negative double resonance signals. In the mixture of nitromethane and methanol, proton transfer was observed in both directions. There are two possible interpretations of this result: (A) one

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(14) F. Kaplan, *J. Amer. Chem. Soc.*, 90, 4483 (1968).

Table V. Proton Transfer Reactions Observed in Nitromethane Mixtures[a]

Nitromethane mixed with	Proton transfer reaction	Limit on PA(CH_3NO_2)[b]
Acetone	$CH_3NO_2H^+ + CH_3COCH_3 \rightarrow (CH_3)_2C{=}O^+H + CH_3NO_2$	<190
Acetaldehyde	$CH_3NO_2H^+ + CH_3CHO \rightarrow CH_3CHOH^+ + CH_3NO_2$	<183
Propylene	$C_3H_7^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + C_3H_6$	>179
	$C_3H_6\cdot^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + C_3H_5\cdot$	>178
Hydrogen sulfide	$H_3S^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + H_2S$	>170
	$H_2S\cdot^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + HS\cdot$	>165
Methanol	$CH_3OH_2^+ + CH_3NO_2 \rightarrow CH_3NO_2H^+ + CH_3OH$	
	$CH_3NO_2H^+ + CH_3OH \rightarrow CH_3OH_2^+ + CH_3NO_2$	≅180

[a] All reactions shown had negative double resonance signals. [b] Values in kcal/mol from ref 15.

Table VI. Proton Transfer Reactions Observed in Nitroethane Mixture[a]

Nitroethane mixed with	Proton transfer reaction	Limit on PA($C_2H_5NO_2$)[b]
Acetone	$C_2H_5NO_2H^+ + CH_3COCH_3 \rightarrow (CH_3)_2C{=}O^+H + C_2H_5NO_2$	<190
Acetaldehyde	$CH_3CHOH^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2H^+ + CH_3CHO$	>183
Propylene	$C_3H_7^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2H^+ + C_3H_6$	>179
Acetonitrile	$C_2H_5NO_2H^+ + CH_3CN \rightarrow CH_3CNH^+ + C_2H_5NO_2$	<186
Ethanol	$C_2H_5NO_2H^+ + C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5NO_2$	<186
Propionaldehyde	$C_2H_5NO_2H^+ + C_2H_5CHO \rightarrow C_2H_5CHOH^+ + C_2H_5NO_2$	<186
Nitromethane	$CH_3NO_2H^+ + C_2H_5NO_2 \rightarrow C_2H_5NO_2H^+ + CH_3NO_2$	>180

[a] All reactions shown had negative double resonance signals. [b] Values in kcal/mol from ref 15.

of the reactions occurs solely because of the presence of excited (nonthermal) ions which contain enough internal energy to undergo an otherwise endothermic reaction, or (B) the proton affinities of the two neutrals are so nearly equal that the Maxwell–Boltzmann thermal energy distribution provides a significant fraction of ion-neutral collisions with enough internal and translational energy to undergo the "endothermic" reaction. Since the center-of-mass translational energy alone is about 0.9 kcal/mol at 300°K, either of these interpretations are reasonable; however, the results for the other mixtures suggest that in this case the second is probably correct.

All of the reactions in Table V are consistent with a value of 180 kcal/mol for the proton affinity in nitromethane which gives $\Delta H_f(CH_3NO_2H^+) = 168$ kcal/mol and $HA(CH_3NO_2^+) = 122$ kcal/mol.

Table VI lists the proton transfer reactions observed in a nitroethane mixture together with the limits they place on $PA(C_2H_5NO_2)$. The fact that nitroethane transfers a proton to ethanol, acetonitrile, and propionaldehyde sets an upper limit of 186 kcal/mol on $PA(C_2H_5NO_2)$ while proton transfer from acetaldehyde to nitroethane sets a lower limit of 183 kcal/mol. We therefore assign $PA(C_2H_5NO_2) = 185$ kcal/mol from which we calculate $\Delta H_f(C_2H_5NO_2H^+) = 157$ kcal/mol and $HA(C_2H_5NO_2^+) = 122$ kcal/mol.

Accurate determinations of proton affinities from observations of proton transfer reactions requires that the proton affinities of the reference compounds be accurately known. In this study we have used the proton affinities assigned by Beauchamp,[15] and all of the proton transfer reactions observed by us are in agreement with his values. In addition to the reactions reported in Tables V and VI and in previous work,[7a] we examined the proton transfer reactions in several additional mixtures in order to establish the following ordering of proton affinities: $C_3H_6 < MeOH \cong CH_3NO_2 < EtONO_2 < MeCHO < EtNO_2 < EtCHO$. A reasonable estimate of the errors in the absolute values of proton affinities is ±4 kcal/mol. Thus the relative values are more significant for compounds such as these with small differences in proton affinities.

Experimental Section

The Varian V-5900 icr spectrometers used in this work have been described in detail previously.[7a,8] The electron beam current was usually about 0.1 μA and was adjusted to give a total ion current of 2×10^{-11} A. Typical operating parameters were: trapping, 0.30 V; source drift, 0.30 V/cm; analyzer drift, 0.10 V/cm. The electron energy was usually set at 30 eV, but the proton transfer reactions used to determine the proton affinities were run at the lowest electron energy possible consistent with good signal-to-noise (12 eV or less).

Nitromethane-d_3 was obtained from Diaprep Inc., Atlanta, Ga. Nitroethane-d_5 was prepared by converting ethanol-d_6 (Stohler) to ethyl-d_5 iodide using red phosphorus and iodine.[16] Treating the iodide with silver nitrate gave[17] nitroethane-d_5 containing 10% of the d_4 material. Nitromethane-^{15}N was obtained by converting sodium nitrite-^{15}N to the silver salt[18] which was then treated with methyl iodide.[17]

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(15) J. L. Beauchamp, *Ann. Rev. Phys. Chem.*, 22, 527 (1971).

(16) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p 284.

(17) N. Kornblum, *Org. React.*, 12, 101 (1962).

(18) N. Kornblum and H. E. Ungnade, "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 725.