l and 2 is striking. An understanding would involve at a minimum some knowledge of metal-ligand bond strengths in complexes **2**, **3**, **6**, and **7**.

Most studies of C-H activation have focussed on aromatic and aliphatic hydrocarbons. In the equally important activation of olefins, the relative stability of $L_nM(H)(CH{=}CH_2)$ and $L_nM(\eta^2\text{-}C_2H_4)$ is a central question.

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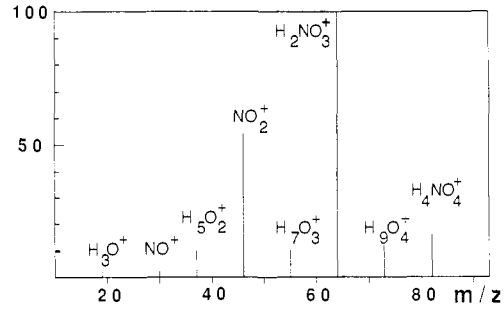

Figure 1. Typical CH_4/CI spectrum of 68% aqueous HNO_3, recorded at ca. 1 Torr, source temperature 40 °C, by using a 5982A Hewlett-Packard quadrupole spectrometer.

Protonated Nitric Acid. Experimental Evidence for the Existence of Two Isomers

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Relatively little is known about the positive ion chemistry of HNO_3, e.g., its proton affinity (PA) is reported to be intermediate between those of H_2O and NH_3, which amounts to an uncertainty of almost 40 kcal mol^{-1}.[1] We have investigated by Fourier-transform (FT-ICR) and chemical ionization (CI) mass spectrometry, using H_3^+, CH_5^+, and H_3O^+ as the ionic reactants, the process

$$HNO_3 + AH^+ \rightarrow \underset{\mathbf{1}}{H_2NO_3^+} + A \qquad (1)$$

previously studied in a flowing afterglow.[2,3] Occurrence of reaction 1 has unequivocally been established by triple-resonance ICR experiments, demonstrating, in addition, slow decomposition of **1** into NO_2^+ and NO^+.[4] The CH_4/CI spectrum of aqueous HNO_3 displays **1** as the predominant peak, together with its hydrate, NO_2^+, and NO^+ (Figure 1).[5] Since the basicity of HNO_3 is hardly accessible to equilibrium measurements owing to the decomposition of **1** under ICR conditions, we resorted to the less reliable "bracketing" technique,[1] in experiments carried out either on isolated ions by FT-ICR spectrometry or by CIMS. The basicity of HNO_3 falls between those of H_2O and of CF_3COOH (or CF_3CH_2OH), leading to an estimated $PA(HNO_3) = 168 \pm 2$ kcal mol^{-1}, not inconsistent with recent theoretical results.[6] From the PA value, one can derive ΔH_f° $(H_2NO_3^+) \approx 166$ kcal mol^{-1}, hence $D(NO_2^+\text{-}H_2O) \approx 10$ kcal mol^{-1}, and $-\Delta H_{(1)} \approx 67$ (A = H_2), 36 (A = CH_4), and ≈ 2 (A = H_2O) kcal mol^{-1}.[1]

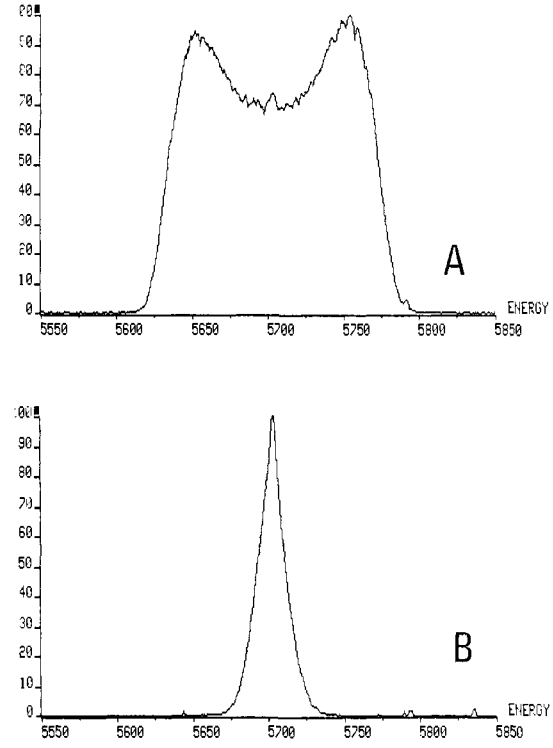

Figure 2. (A) Metastable peak due to the loss of water from ions of type II prepared according to process 1, A = CH_4, in methane at ca. 0.1 Torr. (B) Same peak from ions of type I, obtained by process 2, A = CH_4, in methane at ca. 1 Torr.

We have exploited as well another long-known[7] route to **1**:

$$C_2H_5ONO_2 + AH^+ \rightarrow H_2NO_3^+ + C_2H_4 + A \qquad (2)$$

a process exothermic by ca. 18 (A = CH_4) and 50 (A = H_2) kcal mol^{-1}.

Structurally diagnostic techniques provide strong and mutually supporting evidence for the existence of two isomers of **1**, isomer I being detectable in the ionic populations from reactions of low exothermicity, i.e., from (1), A = H_2O, and (2), A = CH_4, while isomer II is detectable only as a product from highly exothermic processes, i.e., from (1), A = H_2 or CH_4, and (2), A = H_2, under conditions of inefficient collisional deactivation.[8] Structural discrimination between I and II is based on the following evidence.

(1) All thermochemical data are taken from the compilation of Lias et al. (Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695).

(2) Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1973**, *59*, 6272.

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(4) The ICR spectra were recorded with a Nicolet FTMS 1000 instrument, measuring the sample pressure with a Granville-Phillips 280 Bayard-Alpert ion gauge, at a typical resolution of 10^3 fwhh at mass 100, with a trapping voltage of 1.0 V, electron-beam energy 15 eV, under a total pressure of ca. 4×10^{-7} Torr.

(5) $H^+(HNO_3)_x(H_2O)_y$ clusters have been reported, see: Kay, B. D.; Hermann, V.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1981**, *80*, 469 and references therein.

(6) According to 6-31G**//44-31G SCF calculations by Nguyen et al. (Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1984**, 2043), the PA of HNO_3 exceeds that of H_2O by ca. 1 kcal mol^{-1}. Such results, while internally consistent, overestimate absolute basicities, e.g., the calculated $PA(H_2O)$ exceeds the experimental value by some 13 kcal mol^{-1}, which could affect the calculated $D(NO_2^+\text{-}H_2O)$ energy.

(7) Nixon, W. B.; Bursey, M. M. *Tetrahedron* **1970**, *50*, 4389.

(8) These observations do not imply that II is the only or the most abundant isomer formed whenever the protonation process is highly exothermic but simply that only under the specified set of conditions it becomes detectable by MIKE and CID spectrometry. Such structurally diagnostic techniques detect the fraction of the ions that undergo unimolecular or collisionally induced decomposition in the appropriate regions of the spectrometer, rather than sampling the relative ionic abundances in the ion source.

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(i) Irrespective of their source, metastable decomposition of ions II into NO_2^+ and H_2O occurs with a large release of kinetic energy (747 ± 10 meV), giving a typical, dish-topped peak (Figure 2A), while ions I decompose giving an non-Gaussian peak with a much lower kinetic energy release (Figure 2B). Such a difference is particularly significant, in that kinetic energy release is primarily dependent on the reverse activation energy not on the internal energy of the decomposing ions.[9] Large releases are typical of rearrangements, while simple bond cleavages have little or no reverse activation energies.[10] It follows that II must undergo rearrangement prior to metastable H_2O loss, which is not the case of I.

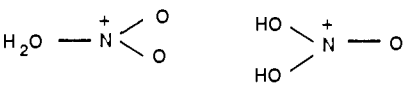
(ii) The collisional-induced dissociation (CID) spectra, depurated from the unimolecular contribution, are also largely different, the CID spectrum of I displaying three fragments, i.e., H_2O^+, NO^+, and NO_2^+, in the approximate 0.7:1:9 ratio, while that of II displays only NO^+ and NO_2^+ in the approximate 1:2 ratio.

(iii) Further structural discrimination is provided by the different metastable decomposition of the ions from the reaction

$$H_2NO_3^+ + H_2{}^{18}O \rightarrow H_2NO_2{}^{18}O^+ + H_2O \qquad (3)$$

unequivocally established by FT-ICR spectrometry and occurring as well under CI conditions.[11] Ions I from (3) undergo metastable decomposition into *unlabeled* NO_2^+, losing exclusively $H_2{}^{18}O$, while labeled ions II undergo nearly statistical (typically 2.5:1) metastable loss of H_2O and of $H_2{}^{18}O$.[12]

Overall, the above results suggest that I is the more stable isomer, characterized by a hydrated nitronium ion structure, whose metastable loss of water involves a simple bond cleavage, without a large release of kinetic energy. The presence of a discrete H_2O



I II

moiety accords well with the selective loss of $H_2{}^{18}O$ in the metastable decomposition of ions I from process (3), that amounts, in this case, to a simple ligand exchange. The features of ions II are consistent instead with a structure containing two OH groups, whose metastable decomposition into NO_2^+ and H_2O presupposes molecular reorganization, which justifies the large release of kinetic energy. The mixed isotopic composition of water from the metastable decomposition of ^{18}O-labeled ions II accords well with a structure containing no O atom in a preexistent H–O–H group, whose loss can occur preferentially, as from I, via a simple bond cleavage, requiring no preliminary rearrangement.

Our conclusions qualitatively agree with the results of SCF calculations, which identify a H_2O–NO_2^+ structure as the most stable among the isomers investigated, showing that the relative energies of ions akin to II are higher by at least 8 kcal mol^{-1}.[6]

It should lastly be noted that the kinetic energy release from II sets a lower limit of the order of 20 kcal mol^{-1} to the activation energy for the hydration of NO_2^+ yielding II and that there are reasons to believe that the free energy of activation for the II → I isomerization is correspondingly large. Remarkably, the process does not appear to be catalyzed by interaction of II with a water molecule.

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(11) Even under CI conditions, $H_2NO_2{}^{18}O^+$ ions arise exclusively from exchange 3, since no appreciable hydration of NO_2^+ has been detected in specific control experiments.
(12) The MIKE and CID spectra were recorded by using a ZAB-2F instrument (Micromass, Ltd.), operating the CI source at 160 °C. The spectra represent an average of 100 scans, with an energy resolution of 1.2 eV main-beam width.

Measurement of ^1H–^1H Coupling Constants in Oligonucleotides by 2D NMR: Application of ω_1-Decoupling

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Three-bond ^1H–^1H coupling constants constitute the basic input for the determination of conformation of d-ribose rings in oligonucleotides by NMR spectroscopy.[1] Different techniques, such as ω_1-scaled COSY,[2,3] P.E.COSY,[4] and DISCO,[5] to name a few, have been used to derive this structural information.[6-9] While all these have proved extremely useful, any procedure that enhances resolution in the spectra is always a welcome addition. In this context ω_1-decoupling in correlated spectroscopy[10,11] is an attractive proposition since this allows complete elimination of multiplicity along the ω_1-axis of the two-dimensional spectrum. In this communication we use the following experimental scheme.[11]

$$90 - (\Delta + t_1)/2 - 180 - (\Delta - t_1)/2 - 90 - \text{acquire}(t_2)$$

t_1 and t_2 are the usual evolution and detection periods, and Δ is a constant time period. In this scheme the heteronuclear H–P coupling will however be retained along the ω_1-axis of the two-dimensional spectrum. The cross peaks can be phased to pure absorption along both axes, while diagonal peaks will have disperse character along ω_2 and absorptive character along ω_1.

Figure 1 shows the (H1′)–(H2′, H2″) cross peak region of the ω_1-decoupled COSY spectrum of the oligonucleotide hairpin d(C-G-C-G-A-G-T-T-G-T-C-G-C-G). It is seen that all the expected cross peaks are present. Both positive (+) and negative (−) signals have been plotted, and the multiplet pattern along ω_2 is + − + − for H1′–H2″ cross peaks and + + − − for H1′–H2′ cross peaks. In the case of nucleotide units G2, G4, G6, G9, and G12, strong coupling artefacts are seen between the H1′–H2′ and H1′–H2″ cross peaks. In Figure 2 a particular horizontal slice through the spectrum in Figure 1 is shown in order to bring out the characteristics of the spectrum. The central + and − signals have lower intensities compared to the two outer signals; the intensity difference being more pronounced in G6. This is a consequence of (i) partial cancellation of the + − intensiteis in the center and (ii) strong coupling effects in G6 because of which the central two lines have lower intensities inherently. All the cross peak multiplets have been simulated (illustrated on the side in Figure 1) to obtain true peak positions which directly yielded the H1′–H2′ and H1′–H2″ coupling constants in all units except where strong coupling effects were observed. In the strongly coupled cases, the simulated peak positions do not yield directly the coupling constant values.

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