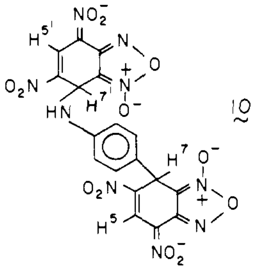
studied previously[5] is that in the latter case a tertiary base (Et_3N or DABCO) is required for transformation to the σ complex to be effective; formation of the zwitterionic intermediate is sufficiently disfavored such that the overall process with aniline alone does not occur. This contrasting behavior reflects the greater stability of σ complexes in the 4,6-dinitrobenzofuroxan system.[9]

Following the characterization of complexes **6**, **8**, and **9**, it became of interest to determine whether a σ complex containing both carbon- and nitrogen-bonding functions could be prepared. In fact, we found that the diadduct **10** can easily be prepared by



10

addition of **4** to a $(CD_3)_2SO$ solution of **8**, followed by 2 equiv of Et_3N. The NMR spectrum of the product is completely in accord with the structural formulation in **10**.[6]

We intend to further investigate the reactions of aromatic amines with various nitroaromatic compounds in order to attempt to delineate the structural/electronic factors with respect to the nucleophile *and* electrophile on ambident reactivity in such systems.

Acknowledgment. Support of this research by grants from the Naval Surface Weapons Center at Silver Springs, MD (M.J.S.), and the Natural Sciences Research Council of Canada (E.B.) is gratefully acknowledged.

Registry No. 4, 5128-28-9; **6**, 84802-77-7; **8**, 84802-78-8; **9**, 84802-79-9; **10**, 84802-80-2; aniline, 62-53-3.

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[9] (a) Terrier, F.; Millot, F.; Norris, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 5883. (b) Buncel, E.; Chuaqui-Offermanns, N.; Norris, A. R.; *J. Chem. Soc., Perkin Trans. 1* **1977**, 415. (c) Buncel, E.; Chuaqui-Offermanns, N.; Moir, R. Y.; Norris, A. R. *Can. J. Chem.* **1979**, *57*, 494.

Formation of the NH_4^- Ion in the Gas Phase

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As part of our interest in gas-phase hydride-transfer reactions[1] we recently observed H_3O^- formed by oxidation of formaldehyde by OH^-.[2] Deuterium-labeling experiments have shown that the structure of the H_3O^- ion can best be desribed as a hydride ion solvated by a water molecule, in agreement with recent ab initio molecular orbital calculations at the 4-31++G level.[3] Equation 1 rationalizes the formation of this species via a two-step process in the collision complex.[2] The first step is proton transfer from

$$OH^- + CH_2O \rightleftarrows [OH^-\cdot CH_2O]^* \rightleftarrows \underset{a}{[H_2O\cdot HCO^-]^*} \rightleftarrows [H^-\cdot H_2O\cdot CO]^* \rightarrow H^-\cdot H_2O + CO \quad (1)$$

formaldehyde to OH^-, but the resulting complex a does not dissociate, because water is more acidic than formaldehyde.[4] The second step is transfer of a hydride from HCO^- to water, resulting in H_3O^- and CO.

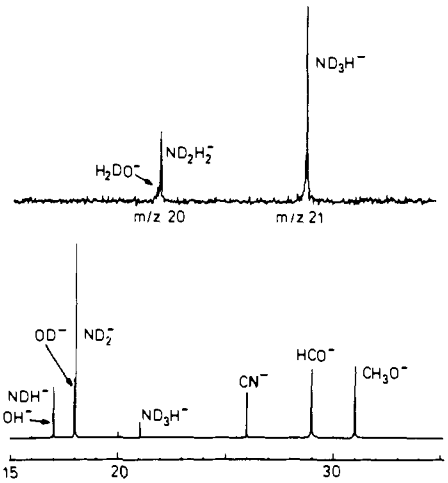

Figure 1. FT ICR spectrum of an $ND_2^-/ND_3/CH_2O$ system. Experimental conditions: $p(ND_3) = 70\ \mu Pa$, $p(CH_2O) = 30\ \mu Pa$, magnetic field strength 1.4 T, electron energy 4.5 eV, emission current 800 nA. The spectrum is taken at a trapping time of 150 ms (i.e., 150 ms after the electron beam pulse started), 2350 transients accumulated. The expanded graph on top shows the mass region from m/z 19 to 22. The OH^- and OD^- ions observed are due to background water but do not interfere with the measurements as can be seen from the low abundance of the H_2DO^- ions.

The observation of H_3O^{-5} raises the question whether NH_4^- can also be generated as a stable species in the gas phase. The reaction between NH_2^- and formaldehyde has been examined earlier by drift cell ion cyclotron resonance spectrometry,[4] but no ion corresponding to NH_4^- has been reported. However, under the improved experimental conditions of our Fourier transform ion cyclotron resonance (FTICR) spectrometer[6,7] we have been able to observe ions at m/z 18. Although our instrument does not yet have the capability of performing high-resolution experiments, the mass of these ions can be measured with sufficient accuracy: 18.0350 ± 0.0037 daltons (exact mass of NH_4^- is 18.0344 daltons). Support for the formation of NH_4^- is derived from the observation that ions at m/z 19 are formed if $^{15}NH_3$ is used.[8] The mass of these ions is measured to be 19.0316 ± 0.0041 daltons (exact mass of $^{15}NH_4^-$ is 19.0314 daltons). This clearly shows that NH_4^- is a stable species in the gas phase.

The mechanism of formation of NH_4^- appears to be different from that of H_3O^- (see eq 1) in the following sense: the proton abstraction from formaldehyde by NH_2^-, which is a stronger base than OH^-, is now exothermic and results in the formation of HCO^- ions (eq 2).[4] Ejection of these HCO^- ions[9] results in removal

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[†] Visiting scientist from the Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50 Finland.

[1] (a) Ingemann, S.; Kleingeld, J. C.; Nibbering, N. M. M. *J. Chem. Soc., Chem. Commun.* **1982**, 1009-1011. (b) Ingemann, S.; Kleingeld, J. C.; Nibbering, N. M. M., presented at the NATO Advanced Study Institute on Chemistry of Ions in the Gas Phase, Vimeiro, Portugal, Sept 1982. The proceedings of this conference will be published as a volume in the NATO ASI series.

[2] Kleingeld, J. C.; Nibbering, N. M. M. *Int. J. Mass. Spectrom. Ion Phys.* **1983**, *49*, 311-318.

[3] Squires, R. R., personal communication.

[4] Karpas, Z.; Klein, F. S. *Int. J. Mass. Spectrom Ion Phys.* **1975**, *18*, 65-68.

[5] H_3O^- has also been observed in an ion-beam experiment: Paulson, J. F.; Henchman, M. J. *Bull. Am. Phys. Soc.* **1982**, *27*, 108.

[6] (a) Comisarow, M. B. In "Transform Techniques in Chemistry"; Griffiths, P. R., Ed.; Plenum Press: New York, 1978; Chapter 10, pp 257-284. (b) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A-1676A.

[7] The general operating procedures for the FT ICR instrument have been described in the following: (a) Kleingeld, J. C.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1982**, *17*, 136-139. (b) Ingemann, S.; Nibbering, N. M. M.; Sullivan, S. A.; DePuy, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 6520-6527.

[8] $^{15}NH_3$ was generated from $[^{15}N_2]$ ammonium sulfate (label content 96.5 atom % ^{15}N).

0002-7863/83/1505-2474$01.50/0

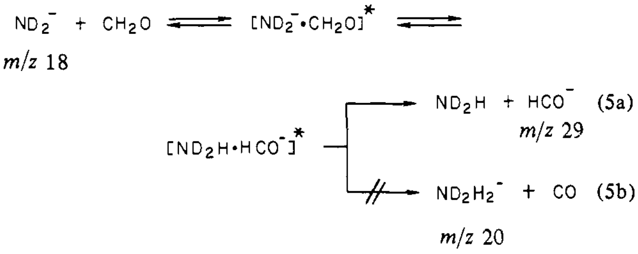
$$NH_2^- + CH_2O \rightarrow \underset{m/z\ 16}{} NH_3 + \underset{m/z\ 29}{HCO^-} \qquad (2)$$

$$HCO^- + NH_3 \rightarrow CO + \underset{m/z\ 18}{NH_4^-} \qquad (3)$$

of the NH_4^- ions, which indicates that in a subsequent ion/molecule reaction a hydride is transferred from HCO^- to ammonia[10] (eq 3). This is further supported by the observation that in the $ND_2^-/ND_3/CH_2O$ system mainly ND_3H^- is formed (eq 4; see Figure 1). The $ND_2H_2^-$ ion observed is due to incomplete

$$HCO^- + ND_3 \rightarrow CO + \underset{m/z\ 21}{ND_3H^-} \qquad (4)$$

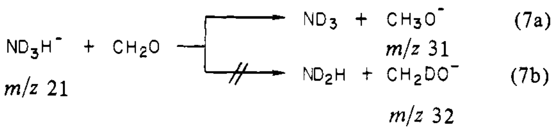
labeling of the ND_3 used rather than to the occurrence of a reaction analogous to the one that forms H_3O^- (eq 1). In agreement with this, NH_3D^- is formed exclusively in the $NH_2^-/NH_3/CD_2O$ system.[11]



Information concerning the structure of the NH_4^- ion can be derived from its reaction with formaldehyde:

$$\underset{m/z\ 18}{NH_4^-} + CH_2O \rightarrow NH_3 + \underset{m/z\ 31}{CH_3O^-} \qquad (6)$$

The ND_3H^- ion is observed to transfer only a hydride ion, not a deuteride ion, to formaldehyde (eq 7). This is shown by ejection of the ND_3H^- ions, which results in a partial decrease of the abundance of the CH_3O^- ions.[12] Conversely, the NH_3D^- ion only transfers the D^- ion to formaldehyde.



These observations show that the hydrogen and deuterium atoms in the ND_3H^- and NH_3D^- ions do not become equivalent. The observed ions can therefore best be described as a hydride ion solvated by an ammonia molecule: $H^-{\cdot}NH_3$. This is in agreement with recent ab initio molecular orbital calculations at the 4-31++G level on NH_4^-, which indicate that the $H^-{\cdot}NH_3$ structure is more stable than the $H_2{\cdot}NH_2^-$ structure[3].

It is possible to bracket the heat of formation of NH_4^- on the basis of the observed reactions. An upper limit of about +85 kJ·mol^{-1} can be calculated from eq 3,[13,14] and a lower limit of −80 kJ·mol^{-1} can be derived from eq 6.[13,15] The calculated[3] heat of formation of the $H^-{\cdot}NH_3$ structure is about +85 kJ·mol^{-1}, in agreement with the present experiments.

The HCO^- ion has been observed to transfer a hydride ion to methylamine and ethylamine as well (eq 8). No hydride transfer

$$HCO^- + RNH_2 \rightarrow CO + RNH_3^- \qquad (8)$$
$$R = H,\ CH_3,\ C_2H_5$$

to dimethylamine has been observed, probably due to the competition of a fast proton-transfer reaction leading to $(CH_3)_2N^-$.

Acknowledgment. We thank Prof. R. R. Squires (Purdue University, IN) and Prof. P. v. R. Schleyer (Universität Erlangen-Nürnberg, West Germany) for stimulating discussions and the Netherlands Organization for Pure Research (SON/ZWO) for financial support. J.E.J. also thanks the Ministry of Education of the Netherlands and the Foundation of the University of Turku for a travel grant.

Registry No. NH_4^-, 12325-21-2; HCO^-, 57340-31-5; ND_3H^-, 84809-69-8; ammonia, 7664-41-7; methylamine, 74-89-5; ethylamine, 75-04-7.

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(9) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413–416.

(10) For other examples of gas-phase hydride-transfer reactions, see: (a) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433–1440. (b) DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *Ibid.* **1978**, *100*, 2920–2922. (c) Schmitt, R. J.; Bierbaum, V. M.; DePuy, C. H. *Ibid.* **1979**, *101*, 6443–6445. (d) Bartmess, J. E. *Ibid.* **1980**, *102*, 2483–2484.

(11) CD_2O was generated by depolymerization of perdeuteroparaformaldehyde (purchased from Merck).

(12) The CH_3O^- ions are also formed by a hydride ion transfer from HCO^- to formaldehyde; see ref 4.

(13) Heats of formation of neutral molecules have been taken from the following: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

(14) The heat of formation of HCO^- has been taken from the value calculated by the following: Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612–5614.

(15) The heat of formation of CH_3O^- has been taken from the following: Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11, pp 87–121.

Double Isotope Fractionation: Test for Concertedness and for Transition-State Dominance

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Most chemical transformations involve the making and breaking of more than one bond, and the question of the timing of these events arises frequently. We report here a possible solution to this problem, in which the isotopic fractionation at one site (e.g., the bond-making site) is measured as a function of the isotope at the other (e.g., the bond-breaking site). This approach, a "double fractionation" experiment, can be used not only to test for concertedness but also to discover whether the isotopically sensitive transition state(s) are fully rate determining. The experiment is general, provided that substitution at one site (e.g., of D for H) can be specified while the fractionation at the other site (e.g., of H vs. D, ^{12}C vs. ^{13}C, or ^{16}O vs. ^{18}O) is measured.

We illustrate the method with the enzyme proline racemase,[1] which proceeds by a "two-base" mechanism (Figures 1 and 2).[2] From experiments with D-[2-^{2}H]- and L-[2-^{2}H]proline,[2,3] it is known that the transition state(s) for substrate interconversion involve kinetically significant proton motion at both protonic sites and that both protons are sequestered on their sites until the proline is released.[4] Let us first assume that the reaction is stepwise (Figure 1). In the first step the C-2 proton of D-proline (H″) is abstracted to give a carbanionic intermediate, and in the second step L-proline is formed by delivery of a solvent-derived proton (H′) to this carbanion. If the reaction is run in mixed H_2O–D_2O then because transition-state 2 is kinetically significant, there will be discrimination against deuterium, and the product L-proline will have a lower deuterium content than the solvent. The product

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[†] Harvard University.

[‡] Imperial College.

[§] National Science Foundation Predoctoral Fellow.

(1) Belasco, J. G. Ph.D. Thesis, Harvard University, 1980. The enzyme was purified to homogeneity by Dr. L. M. Fisher, from *Clostridium sticklandii*.[2]

(2) (a) Cardinale, G. J.; Abeles, R. H. *Biochemistry* **1968**, *7*, 3970–3978. (b) Rudnick, G.; Abeles, R. H. *Ibid.* **1975**, *14*, 4515–4522.

(3) L. M. Fisher, unpublished experiments.

(4) The observed deuterium isotope effects on k_{cat}/K_m are 3.2 (for L-[2-^{2}H]proline) and 2.7 (for D-[2-^{2}H]proline).