Direct Observation of the $H_2NO_2^-$ Ion

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The structure of the gaseous $H_2NO_2^-$ ion in the negative chemical ionisation mass spectrum of butyl nitrate is suggested by charge-reversal chemical-activation mass spectrometry and confirmed by calculation at the 4–31G level.

Orthohyponitrous acid, H_3NO_2, is unknown. The hyponitrous acid that is known in solution is a dimer $HON=NOH$[1] of NOH, whose salts have been long known.[2-5] Taking the putative anion in these salts, the negative molecular ion of nitric oxide, as metahyponitrite ion, we report the direct observation of its hydrated form, using techniques similar to those by which monomeric metaphosphate, PO_3^-, was first observed.[6]

The production of ions by negative chemical ionisation mass spectrometry is a low-energy process,[7] electrons being nearly thermalised in collisions with buffer gas so that stable gaseous negative ions can be formed. With so little excess of energy the few fragmentations that are observed are more likely to be rearrangements than simple cleavages,[8,9] according to both quasi-equilibrium theory and many experiments with both positive and negative ions.

The retrospective application of this latter rule explained in a qualitative way how an ion of m/z 48 could appear in the negative chemical ionisation spectrum of butyl nitrate (buffer gas, CH_4; observed with ZAB-2F and MS50TA mass spectrometers). The m/z 48 ion is a singlet, assigned the empirical formula $H_2NO_2^-$. In the MS50TA instrument it was possible to perform charge-reversal[10] collisional-activation,[11] [equation (1)] analyses on the highly resolved ion beam of $H_2NO_2^-$ alone. This ion is not merely a negatively charged cluster of NO and H_2O. Such an $[NO \cdot H_2O]^-$ cluster is formed in mix-

tures of NO and H_2O under negative chemical ionisation conditions and, after separation of an $O_3^{\cdot-}$ component by high

$$A\text{-}B^+ + He \rightarrow He + 2e^- + A\text{-}B^+ \qquad (1)$$
$$\downarrow$$
$$A^+ + B$$
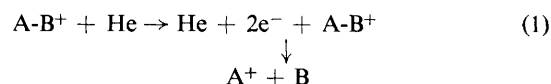
resolution, is shown to decompose in charge-reversal collisional activation only to NO^+ and $H_2O^{\cdot+}$. The $H_2NO_2^-$ ion from nitrate esters has a different charge-reversal collisional-activation spectrum, consisting of major signals at m/z 30 and 32 and very minor ones at m/z 16 and 18 (Figure 1). The knowledge that collisional-activation and charge-reversal collisional-activation spectra are dominated by the products of entropically favourable processes such as simple cleavages and simultaneous loss of adjacent substituents, without regard to the enthalpies of formation of the products,[9] permits discrimination among possible structures of $H_2NO_2^-$. For example, the structure $H_2N\text{-}O\text{-}O^-$ (1) cannot produce NO^+ by this rule. Cleavages can be written to accommodate the observed major products from several other structures, (2)—(4), however. Fragmentation in a collisional-activation process has been found to occur by a scissoring vibration of large amplitude,[12] but the dominant formation of m/z 32 from $(HO)_2N^-$ (2) is not in accord with the electron affinities[13] of NH_2 (0.78 eV, 75 kJ) and O_2 (0.44 eV, 42 kJ); collisional-activation frag-
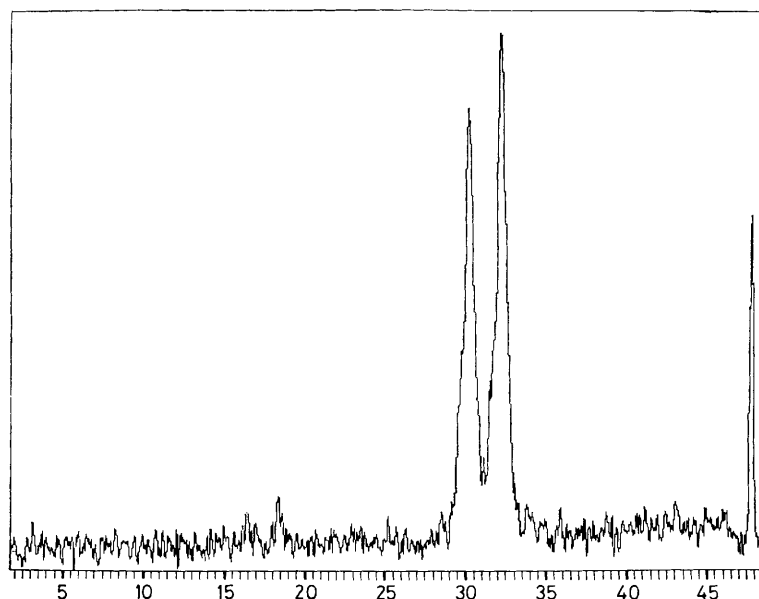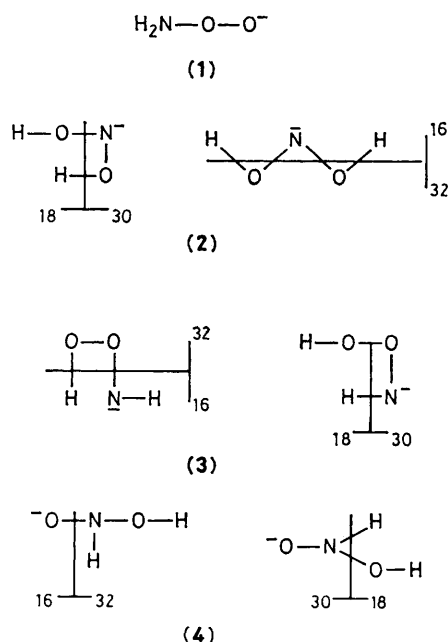

Figure 1. Charge-reversal collisional-activation mass spectrum of the $H_2NO_2^-$ ion.

$$H_2N—O—O^-$$

(1)

(2)

(3)

(4)

ment peaks from thermalised ions should correlate with thermochemical data.[14] The same objection may be made to the fitting of data to the peroxy form HOONH⁻ (3). From such inferences, then, the structure supported by the charge-reversal collisional-activation spectra is the oxygen base HOHNO⁻ (4).

Various computational methods have been successful in confirming experimental rankings of stabilities of neutral species and ions. In particular the 4-31G level of calculation has enjoyed some success in comparison of stabilities of cations and derived anions in isodesmic[15] processes. We have derived ΔH°_{acid}, defined[16] as ΔH°_r for the reaction $HA \rightarrow H^+ + A^-$, for $NH(OH)_2$ as both an oxygen and a nitrogen base by reference to water and ammonia, respectively, equations (2), (3).

$$HO\text{-}NH\text{-}OH + OH^- \rightarrow HO\text{-}NH\text{-}O^- + HOH \quad (2)$$

$$HO\text{-}NH\text{-}OH + NH_2^- \rightarrow (HO)_2N^- + NH_3 \quad (3)$$

The structures of the anions and neutral species minimised at the STO-3G level may be obtained upon request; 4-31G level calculations were performed for these optimised structures. Taking the value of ΔH°_{acid} of water to be 1635 ± 7 kJ

mol⁻¹,[16] we find the oxygen acidity of $NH(OH)_2$ to be 1468 ± 7 kJ mol⁻¹; taking the value of ΔH°_{acid} of ammonia to be 1689 ± 3 kJ mol⁻¹,[17] we find the nitrogen acidity of $NH(OH)_2$ to be 1462 ± 3 kJ mol⁻¹. In confirmation of our spectral interpretation, the nitrogen acidity of the peroxy form H_2NOOH was found to be much weaker, 1519 kJ mol⁻¹. However, the calculations at this level show only that the nitrogen and oxygen acidities of $NH(OH)_2$ are close.

Experimental evidence of the formation of the gaseous orthohyponitrite ion under gentle conditions is therefore at hand, and computational methods are consistent with the structure based upon charge-reversal collisional-activation mass spectra.

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