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RELATIVE NITRYL ION AFFINITIES OF SOME GASEOUS OXYGEN LEWIS BASES BY ION CYCLOTRON RESONANCE

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As part of a continuing study of ionic acylation and related reactions in the gas phase,[1] we have studied the transfer of the nitryl ion, NO_2^+, among the oxygen bases water, formaldehyde, and several alcohols in the gas phase. This study is the first reported examination of relative basicities towards acids (other than H^+) with generally established solution reactivity.

Our system consisted of mixtures of alcohols and alkyl nitrates in an ion cyclotron resonance (icr) spectrometer.[2] At pressures on the order of 40 μtorr (equal contributions from both components) transfer of NO_2^+ from the protonated ester to the alcohol can be observed when ΔH is favorable (eq. 1). In systems containing ethyl nitrate, the reactivity of protonated nitric acid may

$$ROH + R'\overset{+}{\underset{H}{O}}\text{-}NO_2 \rightarrow R\overset{+}{\underset{H}{O}}\text{-}NO_2 + R'OH \qquad (1)$$

also be studied, since the fragmentation of protonated ethyl nitrate to $H_2NO_3^+$ is an important process (eq 2) at the ionizing voltage employed, 30 V. Peak origins were confirmed in each case

$$C_2H_5\overset{+}{\underset{H}{O}}\text{-}NO_2 \rightarrow H\overset{+}{\underset{H}{O}}\text{-}NO_2 + C_2H_4 \qquad (2)$$

by examining the ion cyclotron double resonance[2] signals identifying the precursors of protonated esters. In cases where ambiguity in the identification of peaks would result from similar masses in the icr spectra of the alcohols[2a,3] and the alkyl nitrates,[4] deuterated alcohols (CD_3OD,

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C_2D_5OD) were used.

The following reactions were confirmed by double resonance.

$$H\overset{H}{\underset{+}{O}}NO_2 + MeOH \rightarrow Me\overset{H}{\underset{+}{O}}NO_2 + H_2O \quad (3)$$

$$H\overset{H}{\underset{+}{O}}NO_2 + EtOH \rightarrow Et\overset{H}{\underset{+}{O}}NO_2 + H_2O \quad (4)$$

$$H\overset{H}{\underset{+}{O}}NO_2 + n\text{-}PrOH \rightarrow n\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + H_2O \quad (5)$$

$$H\overset{H}{\underset{+}{O}}NO_2 + i\text{-}PrOH \rightarrow i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + H_2O \quad (6)$$

$$H\overset{H}{\underset{+}{O}}NO_2 + n\text{-}BuOH \rightarrow n\text{-}Bu\overset{H}{\underset{+}{O}}NO_2 + H_2O \quad (7)$$

$$Me\overset{H}{\underset{+}{O}}NO_2 + EtOH \rightarrow Et\overset{H}{\underset{+}{O}}NO_2 + MeOH \quad (8)$$

$$Me\overset{H}{\underset{+}{O}}NO_2 + n\text{-}PrOH \rightarrow n\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + MeOH \quad (9)$$

$$Me\overset{H}{\underset{+}{O}}NO_2 + i\text{-}PrOH \rightarrow i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + MeOH \quad (10)$$

$$Me\overset{H}{\underset{+}{O}}NO_2 + n\text{-}BuOH \rightarrow n\text{-}Bu\overset{H}{\underset{+}{O}}NO_2 + MeOH \quad (11)$$

$$Et\overset{H}{\underset{+}{O}}NO_2 + n\text{-}PrOH \rightarrow n\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + EtOH \quad (12)$$

$$Et\overset{H}{\underset{+}{O}}NO_2 + i\text{-}PrOH \rightarrow i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + EtOH \quad (13)$$

$$Et\overset{H}{\underset{+}{O}}NO_2 + n\text{-}BuOH \rightarrow n\text{-}Bu\overset{H}{\underset{+}{O}}NO_2 + EtOH \quad (14)$$

The absence of the following reactions was confirmed. Other reactions with $i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2$ and higher al-

$$Me\overset{H}{\underset{+}{O}}NO_2 + H_2O \rightarrow \text{no reaction} \quad (15)$$

$$Et\overset{H}{\underset{+}{O}}NO_2 + MeOH \rightarrow \text{no reaction} \quad (16)$$

$$i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + EtOH \rightarrow \text{no reaction} \quad (17)$$

$$i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + MeOH \rightarrow \text{no reaction} \quad (18)$$

$$i\text{-}Pr\overset{H}{\underset{+}{O}}NO_2 + H_2O \rightarrow \text{no reaction} \quad (19)$$

cohols were attempted, but the experiments were inconclusive. From eqs. 3-19, we can construct a nitryl ion affinity scale confirmed for both forward and backward reactions:

$$H_2O < MeOH < EtOH < i\text{-}PrOH$$

$$EtOH < n\text{-}PrOH,\ n\text{-}BuOH$$

The exothermicity of some of the reactions observed may be confirmed by calculation of ΔH using published[4,5] data. Reaction 3 is expected to be exothermic by 25 kcal/mole, reaction 4 by 19 ± 3 kcal/mole, and reaction 8 by 4 ± 3 kcal/mole. The sequence follows the trend expected on the basis

of "substituent polarizability"[6] and resembles what might be expected on the basis of solution reactivity. However, solution reactivities are a poor guide to the true reactivity of unsolvated ions; for example, the acidities of alcohols in the gas phase follow a trend opposite to solution acidities.[7] Recent calculations support this hitherto unsuspected trend.[8]

The fact that the nitryl ion is transferred readily among hydroxyl compounds also supports the conclusion[5a] that the structure written in eq. 1 for the protonated nitrate ester is of lower energy than a form in which a nitro-group oxygen is protonated, $RON(O)OH^+$, as was suggested earlier[4] on the basis of fewer data. The experimental ΔH_f found for protonated ethyl nitrate[4] was intermediate between the values calculated[5a] for the two protonated isomers, and offered no conclusive proof of the correctness of the calculations.

Finally, the nitryl ion affinity of formaldehyde may be placed within this series because of the formation of the appropriate reagent from methyl and ethyl nitrate (eq 20).[9] The nitration of

$$R\text{-}CH_2\text{-}ONO_2^{+\cdot} \rightarrow CH_2{=}\overset{+}{O}\text{-}NO_2 + R\cdot \qquad (20)$$

water by this species does not occur (the reaction is calculated to be endothermic by 32 kcal/mole) but the ion is capable of nitrating methanol and ethanol (eqs. 21, 22), under conditions where space charging in the icr cell is demonstrated not to be important. The accepted heats of formation of the reactants and products suggest that eq 21 is endothermic by 7 kcal/mole and 22 is endothermic by 13 ± 3 kcal/mole. It is possible that a reactant produced by fragmentation and studied by icr may contain enough internal excitation energy to undergo reactions which would be endothermic for ground-state ions. The reverse of eq 21 is in fact also observed, as it should be if it is exothermic. Hence the position of formaldehyde in our list of nitryl ion affinities is close to methanol, but on which side it belongs is unclear. The fact that eq 22 is observed in spite of the calculated endothermicity of 13 kcal/mole may also be explained on this basis, or alternatively

$$CH_2{=}\overset{+}{O}NO_2 + MeOH \rightarrow Me\underset{H}{\overset{+}{O}}NO_2 + CH_2O \qquad (21)$$

$$CH_2{=}\overset{+}{O}NO_2 + EtOH \rightarrow Et\underset{H}{\overset{+}{O}}NO_2 + CH_2O \qquad (22)$$

may point to an error in the published ΔH_f data, since the minimum value at eq 21 is unexpected if one compares the smooth trend of the first series (eqs. 3-19) with it.

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