All these possibilities are obviously strongly dependent on the ordering of the initial $n\pi^*$ and $\pi\pi^*$ triplet states and on their energetic separation in the specific cyclic enone.

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# The Gas-Phase Acidity Order of Some Inorganic Acids

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The gas-phase acidity order at 300 °K of the inorganic acids, water, ammonia, and hydrogen has been directly determined using the flowing afterglow technique. The order established is $H_2O > H_2 > NH_3$, water being the strongest acid in this series. This result is inconsistent with recent calculations, current available thermochemical data, and the order found in solution.

Utilisant une technique continue de luminescence retardée, on détermine directement l'ordre de l'acidité en phase gazeuse à 300 °K d'acides inorganiques, de l'eau, de l'ammoniac et de l'hydrogène. On trouve que l'eau est le produit le plus acide et que l'ordre décroissant est $H_2O > H_2 > NH_3$. Ce résultat n'est pas consistant avec les calculs théoriques récents, les données thermodynamiques disponibles actuellement et l'ordre trouvée en solution.

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As part of a program directed towards the determination of relative acidities of organic acids in the gas phase, experiments were recently performed to determine the gas-phase acidities of some simple inorganic acids. The flowing afterglow technique was employed to investigate the kinetics at 300 °K of proton transfer reactions of the type

$$[1] \qquad X^- + YH \rightleftharpoons Y^- + XH$$

The determination of the preferred direction of proton transfer at thermal energies identifies the sign of the free energy change of reaction 1 which, in turn, provides a measure of the relative gas-phase acidity of the acids YH and XH. Such information is valuable in formulating intrinsic reactivity functions, which should have an important bearing on reactivity functions measured in solution. Proton transfer reactions proceeding in the gas phase represent a limiting behavior that can be employed as a standard against which the performance of proton transfer reactions proceeding in the condensed phase may be related.

The experiments were performed in one of the flowing afterglow systems of the Environmental Science Services Administration Research Laboratories in Boulder, Colorado. Details of the method of operation and data analysis have been thoroughly described elsewhere (1, 2). Helium was again used as the buffer gas. The helium pressure in the tube was typically *ca.* 0.4 Torr. The $NH_2^-$ and $H^-$ ions were generated by 100

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TABLE 1. Summary of acid–base reactions investigated in the gas phase at 300 °K

| Acid–base reaction | $k_f$* | $k_r$* | $K$ | $-\Delta G_{300}{}^0$ (kcal mol$^{-1}$) |
|---|---|---|---|---|
| $H^- + H_2O \rightleftharpoons OH^- + H_2$ | $\gtrsim 5(-11)$ | $< 5(-12)$ | $> 10$ | $> 1.4$ |
| $NH_2^- + H_2O \rightleftharpoons OH^- + NH_3$ | $\gtrsim 5(-11)$ | $< 5(-12)$ | $> 10$ | $> 1.4$ |
| $NH_2^- + H_2 \rightleftharpoons H^- + NH_3$ | $\geqslant 3.7(-11)$ | $\sim 4(-12)$ | $\gtrsim 10$ | $\gtrsim 1.4$ |

*Units in cm$^3$ molecule$^{-1}$ s$^{-1}$, (−11) denotes $10^{-11}$.

and 25 eV electron impact on $NH_3$, respectively. The production of $OH^-$ has been described previously (2). The reactant, $H_2O$, concentration could not be measured by metering it into the flow tube through calibrated flow elements, which is our conventional technique for measuring neutral concentration. The $H_2O$ concentration was therefore measured by monitoring the increase in the total pressure in the reaction region as the vapor was bled into it. This method of measuring $H_2O$ concentration is, however, both insensitive (the smallest partial pressure measurable with capacitance manometer with a 10 Torr sensing head was at best 0.1 microns) and inaccurate. Consequently, the rate constants for the fast reactions involving $H_2O$ are necessarily limits and are considered reliable only to within a factor of 2.

A summary of the kinetic data obtained for this series of experiments is given in Table 1. The measured equilibrium constant, which was taken to be equal to the ratio of the forward and reverse reaction rate constants, will be equal to the thermodynamic equilibrium constant only if the energy distributions of the respective reactants of the forward and backward proton transfer reactions investigated follow Boltzmann energy distributions. We expect that this is the case in this series of experiments since the ionic species are allowed to undergo many thousand collisions with helium atoms before entering the reaction region where the neutral reactant species are added in thermodynamic equilibrium at room temperature. Thus the data shown in Table 1 clearly indicate the gas-phase acidity order $H_2O > H_2 > NH_3$, water being the strongest acid in this series. Whereas the observation that water is a stronger acid than ammonia in the gas phase has already been reported (3, 4), the position of hydrogen in this sequence has not, to our knowledge, been previously determined.

The gas-phase acidity order determined in this series of experiments is inconsistent with the recent theoretical studies of Ritchie and King who, on the basis of their computations of the potential energy surfaces of proton transfer reactions, predicted both $NH_3$ and $H_2O$ to be stronger acids than $H_2$ (5, 6). The position of $H_2$ in our acidity scale is also inconsistent with the thermochemical data presently available. The value of 4.38 eV for $D(NH_2—H)$ (7) and 1.21 eV for the electron affinity of $NH_2$ (8) are probably least reliable and may be low or high, respectively, by as much as 0.5 eV.[2] Finally, the solution acidity order of this series is $H_2O > NH_3 > H_2$ since metal hydrides undergo facile proton transfer reactions with both water and ammonia to liberate hydrogen in solution (9, 10). Although the exchange reaction between amide and $D_2$ proceeds quite readily in solution, it has been found that the hydride ion is not involved in this exchange process. The reversal of the acidity order of $NH_3$ and $H_2$ in the gas phase suggests that solvation effects favor the right-hand side of the equilibrium

$$NH_3 + H^- \rightleftharpoons NH_2^- + H_2 \qquad [2]$$

Similar acidity order reversals have been shown in the gas phase for alcohols and substituted amines (3, 11).

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[2] Indeed, in the course of this work the authors have become aware of a very recent redetermination of $D(NH_2—H)$ by S. W. Benson, who suggests a value of 4.73 ± 0.04 eV, which is considerably higher than the older value.

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# Utility of Shift Reagents in Nuclear Magnetic Resonance Studies of Polyfunctional Compounds: *N*- and *O*-Acetylated Carbohydrates and Nucleosides

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The utility of n.m.r. shift reagents, $Eu(DPM)_3$ and $Pr(DPM)_3$, can be extended to polyfunctional molecules containing acetate and amide groups with significant spectral simplification and definitive peak assignments based on "signal crossover" phenomena.

On démontre que l'utilité des réactifs $Eu(DPM)_3$ et $Pr(DPM)_3$ qui induisent des déplacements en r.m.n. peut être étendue aux molécules polyfonctionnelles contenant des groupes acétate et amides; il en résulte que les spectres sont simplifiés d'une façon remarquable et que des attributions définitives de pics peuvent être faites.

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Recent work has demonstrated the ability of europium (1, 2) and praseodymium (3) chelates of dipivaloylmethane to produce remarkable shifts in the $^1H$ n.m.r. spectra of monofunctional compounds possessing simple and relatively complex structures (4). We report herein the effects of shift reagents on the n.m.r. spectra (at 100 and 60 MHz) of various classes of *polyfunctional* compounds, in which, *a priori*, multiple sites of complexation would be anticipated. We demonstrate the application of $Eu(DPM)_3$ and $Pr(DPM)_3$ chelates in the assignment of *O*-acetyl and *N*-acetyl resonance signals in polyacetylated carbohydrates as well as in the spectral simplification of various polyfunctional derivatives, including *nucleosides*.

Model studies[4] on the mechanism and preferential sites of complexation of Eu chelates with polyfunctional molecules were performed on methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (6), the corresponding 5-*O*-acetate, and 5-deoxy (7) analogs. The induced shifts decreased as expected in the order $\Delta Eu\text{:}OH > H_{5,5'} > H_4$, $H_3 > H_1$ in accordance with the generalization that protons remote from the site of complexation suffer smaller induced shifts than those of closer proximity (8). The 5-*O*-acetate and 5-deoxy analogs were found to complex to the extent of approximately 40–50% and 10–20% respectively, compared to the parent compound. Upfield shifts of approximately the same relative magnitudes were observed using $Pr(DPM)_3$ in $CCl_4$.

The significant interaction with the 5-*O*-acetate derivative cited above, prompted us to study substrates containing more than one acetyl group. In the case of α- and β-D-glucose pentaacetates, in which the relative chemical shifts of the respective acetyl signals are known by inference with other model compounds (9, 10) and in the case of β-D-galactose pentaacetate, the signal of the *primary* acetoxy group was in each case, shifted substantially more than secondary acetoxy signals. Incremental additions of $Eu(DPM)_3$ in minute portions to a solution of α-D-glucose pentaacetate

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[4] Our initial studies with diacetone glucose revealed that at a defined concentration of $Eu(DPM)_3$ the order of chemical shifts increasing to higher field were $H_5 > H_3 > H_1 > H_4 > H_2 > H_{6,6'}$. Similar results have been reported on this compound while this work was in progress (5). We also note that the presence of two hydroxyl groups in a molecule as in 5-deoxy-1,2-*O*-isopropylidene-D-*xylo*-hexofuranose causes increased broadening of bands and presents some limitation on the method.