

the experimental bands should be completely superimposed, and the spectrum should resemble those of **2** and **3**. The principal point of resemblance between the pleiadienes **1** and **4-8** on the one hand and their heterocyclic analogs **2** and **3** on the other is the constancy of the location of the first strong band at $27,000 \pm 500 \text{ cm}^{-1}$. Since the band seems to be somewhat related to the short-axis polarized "p" band of naphthalene, this indicates that the sulfur atom in the peri position causes similar transverse conjugation as a double bond. Nevertheless, any further spectral analogy appears fortuitous or missing altogether, and this

shows the limitations of the notion of isosterism. Thus, the apparent similarity of the spectra of **1**, **2**, and **3** is much more complex than the simple concept of isosterism would lead one to believe.

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Arrival Time Distributions in High-Pressure Mass Spectrometry. IV. Origin of Linear van't Hoff Plots under Nonequilibrium Conditions in Chemical Ionization Studies of Reversible Ionic Reactions¹

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Abstract: Arrival time measurements in the water system confirm earlier suggestions that, under typical operating conditions, equilibrium in proton hydration is not achieved within the average residence time of ions in chemical ionization sources. Previous evidence cited to support the establishment of equilibrium, the independence of results of water concentration, and the linearity of van't Hoff plots can be understood quantitatively on the basis of a model which recognizes the temperature dependence of ion residence times in the source and derives the apparent equilibrium constant from its operational definition using the kinetics of sequential or of opposing quasi-first-order reactions.

The study of ionic equilibria in the gas phase has received considerable attention during the past few years because of its ability to provide heats of reaction of gaseous ions,²⁻¹³ including those defining intrinsic acidities and basicities, and a better understanding of the solvation process. One system of great interest and

fundamental importance is the hydration of the proton.^{2a,3,5,6,11,12,14} Early investigations based on ion sampling from a field free source at approximately atmospheric pressure^{2,3} led to heats of hydration which were in reasonable agreement with each other, with heats of reaction measured by a collisional detachment technique,¹⁵ and with theoretical calculations based on *ab initio* considerations.¹⁶ However, in a series of extensive investigations using chemical ionization techniques and hydrocarbons as major constituents, under conditions where pressure was on the order of a few Torr and small extraction fields were present, a set of heats of reaction was derived which differed sharply from those reported earlier for the first two hydration steps.^{6,11} The discrepancy is particularly perplexing because independence of water concentration and linearity of van't Hoff plots were unquestionable, and these are frequently accepted as indicators of achievement of equilibrium.

We report here why these criteria are insufficient evidence for the attainment of equilibrium in chemical ionization sources and present a partial resolution of the discrepancies.

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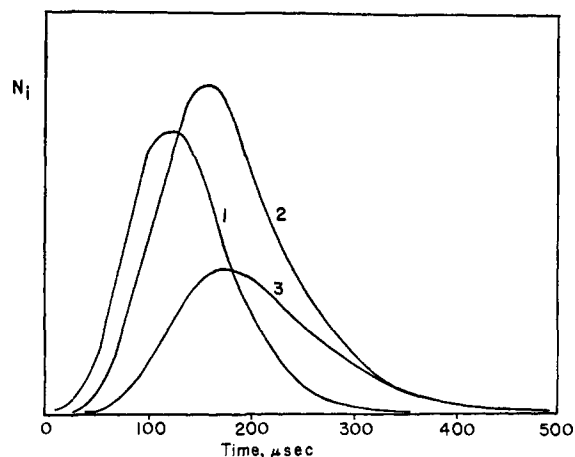


Figure 1. Residence time distributions of H_3O^+ , H_3O_2^+ , and H_7O_3^+ (curves 1, 2, and 3) at a field strength of 3.3 V/cm, 468°K, 0.023 Torr of H_2O , and 0.977 Torr of methane.

Experimental Section

Arrival time distributions were determined using a modified Atlas CH-4 mass spectrometer as described previously¹⁷⁻¹⁹ by providing a 0.1- μsec pulse of electrons which ionizes the gas and gates a time-to-pulse height converter. Ion arrival pulses terminate the converter whose output pulses are sorted on a 400 channel pulse height analyzer, each channel corresponding to an interval of 1.25 μsec . After a few minutes of accumulation, the PHA output is transferred onto paper tape. All data manipulations and calculations are performed on a Univac 1108 computer using the time sharing mode.

Results and Discussion

Figure 1 shows illustrative arrival time distributions of H_3O^+ , H_3O_2^+ , and H_7O_3^+ obtained over various periods and taken directly from the output of the multichannel analyzer. They have been shifted slightly to take into account the variation in transit time in the analyzer as a result of the difference in mass, using eq I. $t(\text{transit})$

$$t(\text{transit}) = c(m/e)^{1/2} \quad (\text{I})$$

may be calculated directly but it is better to evaluate c experimentally and was found to be 1.82 ± 0.01 , at an accelerating potential of 2 kV in good agreement with the value of 1.84 ± 0.06 which may be calculated from an earlier evaluation of c at 3.0 kV.¹⁷

As indicated in Figure 1 equilibrium is not established over the range of times accessible in a typical chemical ionization source since the normalized arrival time distributions of these ions would then be identical.¹⁷ A logarithmic plot (Figure 2) shows convincingly that equilibrium is not achieved even at the largest residence times since the difference does not become constant.¹²

Arrival time distributions of H_3O^+ are dominated by times of less than approximately 200 μsec and those of H_3O_2^+ by times less than 350 microseconds; these periods are much shorter than those required for the establishment of equilibrium. In continuous experiments these portions of the distribution may be expected to dominate the measured ion current; the observed ion current ratio is a time average which can

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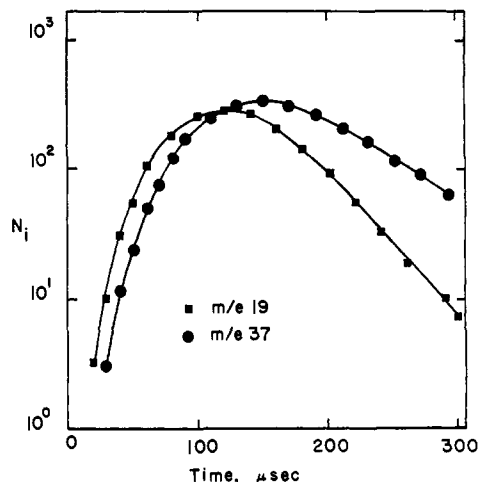
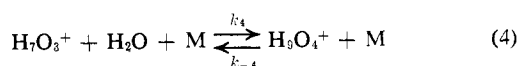
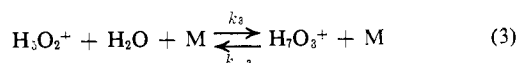
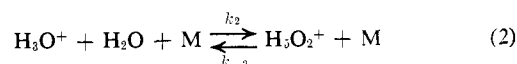
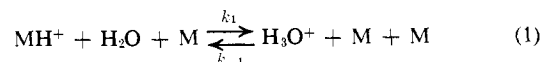


Figure 2. Logarithm of H_3O^+ and H_3O_2^+ ion currents and their dependence on residence time under the same conditions.

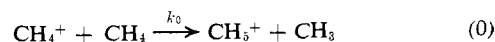
approach the equilibrium value only if the areas under the arrival time distribution curves at times less than those required for the attainment of equilibrium are negligible. Even when the average residence time is somewhat in excess of that required for the attainment of equilibrium, the ion current ratio includes significant time regions where equilibrium is not established and this should lead to incorrect thermodynamic parameters.

Quasi-Thermodynamic Parameters Derived under Conditions of Kinetic Control

The earlier work of Cunningham, *et al.*,¹² as well as Figure 2 clearly demonstrate that at relatively low temperatures the reaction is far from equilibrium but that relative ion intensities are determined instead by the kinetics of the approach to equilibrium. The reaction sequence representing the first few hydration steps is



In pure water, MH^+ is merely H_2O^+ and the position of the equilibrium permits neglect of the reverse reaction; with methane as the major drift gas, MH^+ is CH_5^+ and another reaction step must be included.



In addition to reactions 1-4, each ion is also lost by diffusion to the walls, by extraction from the source, and by neutralization. As long as the diffusion and recombination coefficients are of similar magnitude for all ions involved, these ion loss processes should affect all ions nearly equally. Differences arise from the kinetic behavior which converts initial ions earlier in time so that the mean time during which each ion exists in the source increases as the number of steps

required to produce it increases. For simplicity, we neglect this complication here.

Reactions 1 and 0 cannot be expected to go to equilibrium but must proceed rapidly in the forward direction. With methane as the major drift gas, 99% of the methane ions are converted to methanium ions within 2.2×10^{-7} sec at a pressure of 1 Torr and at 300°K, while the further conversion to H_3O^+ requires an additional 4.8×10^{-6} sec. These estimates are based on $k_0 = 1 \times 10^{-9}$ cm³/sec¹⁷ and $k_1 = 2 \times 10^{-9}$ cm³/sec²⁰ and a concentration of 23 mTorr of water. It follows that the time required for the formation of H_3O^+ is small in comparison to the overall residence times and can be neglected under most conditions. When these periods become substantial, the magnitude of the forward rate constants and their dependence on temperature should become experimentally observable.

In equilibrium studies it has normally been assumed that all other steps, *i.e.*, reactions 2, 3, and 4, are at equilibrium. Because the greatest discrepancies in reported heats, free energies, and entropies of reaction exist for reaction 2, we confine our further considerations to this step.

The operational definition of the equilibrium constant is

$$K_a = [\text{H}_3\text{O}_2^+]/([\text{H}_3\text{O}^+][\text{H}_2\text{O}]) \quad (\text{II})$$

The subscript *a* is used to indicate that the quantity calculated *via* eq II is not necessarily the equilibrium constant *K* but an experimental observable whose relationship to the equilibrium constant is to be established. Relating the ion concentrations in II to observed ion currents already implies the assumption that sampling is nondiscriminatory and that further collision-induced processes, adiabatic cooling near the source exit slit, and other factors are not of importance.

Several approaches may be employed to estimate the effect of residence time, temperature, pressure, and water concentration on the apparent equilibrium constant K_a and the apparent thermodynamic quantities derived from its temperature dependence. The first is based on a model in which reactions 1, 2, and 3 proceed only in the forward direction (complete kinetic control of all reactions) and neglects the time required for formation of the reagent ion MH^+ as justified above. The linear first-order differential equations describing the time-dependent behavior of ion concentrations leads to

$$K_a = \frac{k_2[\text{M}]}{e^{-k_1[\text{M}][\text{H}_2\text{O}]t} - e^{-k_3[\text{M}][\text{H}_2\text{O}]t}} \times \left\{ \frac{e^{-k_1[\text{M}][\text{H}_2\text{O}]t} - e^{-k_3[\text{M}][\text{H}_2\text{O}]t}}{(k_3 - k_1)[\text{M}][\text{H}_2\text{O}]} - \frac{e^{-k_2[\text{M}][\text{H}_2\text{O}]t} - e^{-k_3[\text{M}][\text{H}_2\text{O}]t}}{(k_3 - k_2)[\text{M}][\text{H}_2\text{O}]} \right\} \quad (\text{III})$$

A second approach permitting better physical insight relies on the explicit expressions for the formation and consumption of H_3O^+ and H_3O_2^+ , respectively. If the methanium ion current in the absence of further reactions is designated as $i(\text{MH}^+)$ and the period of MH^+ formation is neglected, one may view the residence time t of the charge in the ion source as divided into

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the lifetime t_1 of the charge as MH^+ , the period t_2 during which it is present in the source as H_3O^+ , and the time t_3 it remains as H_3O_2^+ ; we may now write for the observed ion currents i of H_3O^+ and H_3O_2^+

$$i(\text{H}_3\text{O}^+) = i(\text{MH}^+)(1 - e^{-k_1[\text{M}][\text{H}_2\text{O}]t_1}) \times (e^{-k_2[\text{M}][\text{H}_2\text{O}]t_2}) \quad (\text{IV})$$

$$i(\text{H}_3\text{O}_2^+) = i(\text{MH}^+)(1 - e^{-k_1[\text{M}][\text{H}_2\text{O}]t_1}) \times (1 - e^{-k_2[\text{M}][\text{H}_2\text{O}]t_2})(e^{-k_3[\text{M}][\text{H}_2\text{O}]t_3}) \quad (\text{V})$$

Substitution into eq II clearly shows that the apparent equilibrium constant is independent of the approach to equilibrium of reaction 1

$$K_a = [\text{H}_2\text{O}]^{-1}(1 - e^{-k_2[\text{M}][\text{H}_2\text{O}]t_2}) \times e^{-(k_1[\text{M}][\text{H}_2\text{O}]t_1 - k_3[\text{M}][\text{H}_2\text{O}]t_3)} \quad (\text{VI})$$

The relationships when (IV) and (V) are weighted by appropriate distribution functions for t_1 and t_2 are more complex but lead to a similar general conclusion. In the limit, (VI) reduces to

$$\lim_{t \rightarrow 0} K_a = k_2[\text{M}]t_2 \quad (\text{VII})$$

The kinetics of the approach to equilibrium of two opposing quasi-first-order reactions may be employed as a third method of analysis. It relies on the ability to neglect the details of the steps leading to the formation of H_3O^+ as shown above and implies that all further steps such as reactions 3 and 4 do not materially affect the concentration of H_3O_2^+ . From the differential equation describing reactions 2 and -2 at the steady state at time $t - t_1$, one obtains

$$K_a = K \frac{1 - e^{-(k_2[\text{M}][\text{H}_2\text{O}] + k_{-2}[\text{M}]) (t - t_1)}}{1 + K[\text{H}_2\text{O}]e^{-(k_2[\text{M}][\text{H}_2\text{O}] + k_{-2}[\text{M}]) (t - t_1)}} \quad (\text{VIII})$$

In the limit, this becomes

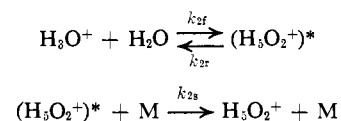
$$\lim_{t \rightarrow 0} K_a = k_2[\text{M}](t - t_1) \quad (\text{IX})$$

This relationship is again independent of the water concentration.

Under the further approximations that $t_2 \gg t_1 + t_3$ or $t \gg t_1$, not inherent in the analysis leading to eq IV, one obtains from (VII) or (IX)

$$\lim_{\substack{t \rightarrow 0 \\ t \gg t_1}} K_a = k_2[\text{M}]t \quad (\text{X})$$

k_2 , of course, does not describe the rate constant of a simple one-step process but must be viewed within the Lindeman formalism



and is, in the low-pressure limit, $k_{2f}k_{2s}/k_{2r}$. The full rate equation

$$d[\text{H}_3\text{O}_2^+]/dt = k_{2f}[\text{H}_3\text{O}^+][\text{H}_2\text{O}]k_{2s}[\text{M}]/(k_{2s}[\text{M}] + k_{2r})$$

shows clearly that the overall rate of reaction 2 cannot exceed the collision rate of H_3O^+ with H_2O , which is about 10^{-9} cm³/sec. If reaction 2s occurs with unit collision efficiency, the lifetime of $(\text{H}_3\text{O}_2^+)^*$ with respect to fragmentation may be estimated as $k_2/k_{2f}k_{2s}$ or $3 \times 10^{-8} \exp(4900/RT)$ sec if the value of k_2 as reported by

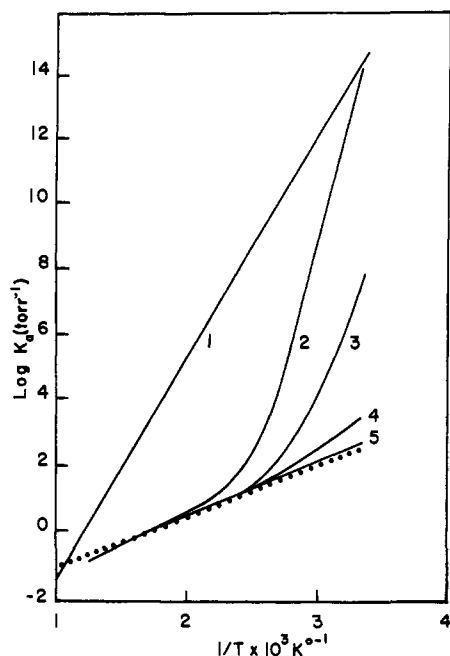


Figure 3. van't Hoff plot of quasi-equilibrium constant K_a calculated from eq VIII and XI for four water pressures: 0.1 Torr of H_2O (curve 2); 0.023 Torr of H_2O (curve 3); 0.005 Torr of H_2O (curve 4); and 0.0007 Torr of H_2O (curve 5) at a third body pressure of 1.0 Torr and $z/E = 0.09$ cm²/V. Curve 1 represents the results of Cunningham, *et al.*,¹² extrapolated to lower temperatures. The slope of the line (· · ·) is that defined by eq X and XI for complete kinetic limitation and no reverse reaction.

Cunningham, *et al.*,¹² is accepted. The magnitude of $k_2[M]$ is on the order of 10^{-10} to 10^{-9} cm³/sec when $[M]$ is 1 Torr,¹² and the forward reaction should therefore be quasi-second order over most of the range of temperatures and pressures of interest and not third order as written. Consequently, the apparent equilibrium constant should also be independent of inert gas concentration; the behavior of K_a under conditions of complete kinetic control is therefore the same as if the system were at equilibrium, that is, K_a is independent of water concentration and inert concentration, two of the major arguments employed in the past to suggest that experimental conditions permit the attainment of equilibrium.

The third argument for the existence of equilibrium has been the linearity of van't Hoff plots. It is clear that eq X may lead to a form which includes a term of the required exponential form through the activation energy of reaction 2 but that the temperature dependence of t must also be evaluated to permit a quantitative interpretation and comparison with experimental data. In the absence of arrival time distribution measurements for work reported by others, mean drift times given by drift theory may be employed, since these have been shown to lead to calculated residence times within a factor of 2 of those experimentally observed.¹⁷⁻¹⁹ The mean residence time \bar{t} is conveniently given by¹⁹

$$\bar{t} = (z/T)(P/E)\sqrt{\alpha\mu} \times 10^{-2} \text{ sec} \quad (\text{XI})$$

where z is the drift length in centimeters, T is in degrees Kelvin, the pressure P of $[M]$ is in Torr, and the repeller or extraction field E is in volts per centimeter; α and μ

are the polarizability and reduced mass in atomic units. For H_3O^+ in CH_4 , $\bar{t} \simeq 0.12(z/T)(P/E)$ sec.

Unfortunately the rate constants k_1 , k_{-1} , k_3 , and k_{-3} are not known sufficiently well to evaluate the temperature dependence of K_a through eq III. While $k_2 = 3.32 \times 10^{-30} e^{4900/RT}$ cm⁶/sec and $k_{-2} = 5.19 \times 10^{-6} e^{-26700/RT}$ cm³/sec are given by Cunningham, *et al.*,¹² the negative activation energy may be associated with a step other than k_{2f} . Since the dependence of the equilibrium on methane concentration in the methane-water system was not investigated experimentally,⁶ we may employ the experimental value of k_2 , also obtained in the methane-water system,¹² to predict K_a and ΔH_a for conditions of chemical ionization. Figure 3 summarizes the calculated quasi-van't Hoff plots based on eq VIII and XI, these rate constants, a drift length z of 0.9 cm, and a field strength of 1 V/cm.

At temperatures in excess of 400°K, all water concentrations less than about 25 mTorr lead to the limiting value of the slope defined by complete kinetic control (eq X). At greater water concentrations, the temperature range over which kinetic control gives a good approximation to the apparent equilibrium constant is reduced.

The limiting value of the apparent heat of reaction ΔH_a can be scaled from Figure 3 but can also be derived explicitly by recognizing that the logarithm of a function is very nearly linearly proportional to its reciprocal over a limited range. Between 300 and 700°K the relationship $\log T = 3.147 - (2.22 \times 10^2/T)$ is obeyed with a deviation of less than 0.5%, even though non-linearity at higher temperatures is clearly evident in Figure 3. Insertion of (XI) and of the ideal gas law into eq X leads to

$$\lim_{t \rightarrow 0} \log K_a = -2 + \log A_2 R P^2 \sqrt{\alpha\mu} (z/E) - 2 \times \log T - [E_2/(2.303RT)] \quad (\text{XII})$$

where A_2 and E_2 are the preexponential factor and activation energy of reaction 2, respectively, and R is the gas constant (1.04×10^{-19} molecules °K Torr⁻¹ cm⁻³). The factor 2 preceding the $\log T$ term arises from the ideal gas law. After substitution

$$\lim_{t \rightarrow 0} \log K_a = 9.8 + \log \left(\frac{A_2 \sqrt{\alpha\mu} P^2 z}{E} \right) - \left(\frac{E_2 - 2025}{2.303RT} \right) \quad (\text{XIII})$$

The apparent heat of reaction ΔH_a obtained from a van't Hoff plot is $E_2 - 2025$ or -6.9 kcal/mol if Kebarle's value¹² for E_2 is employed. A line corresponding to this equation is drawn in Figure 3 and represents the asymptote to the full equation at higher temperatures.

It is of interest to examine the range of validity of eq VIII and X. The requirement that the period of formation of H_3O^+ (*i.e.*, t_1) is small is of concern because it affects the time available for the achievement of equilibrium. Since the rate constants of reactions 0 and 1 are only weakly dependent on temperature, (VIII) and (X) may be expected to predict values of K_a somewhat too high at pressures less than about 0.02 Torr and eq III should then be used. The limit of that relationship at very short times is one half that given by X, so that the error should not exceed a factor of 0.5.

A more serious limitation is the further reaction of

H_2O_2^+ . At temperatures in excess of about 500°K and water pressures larger than a few millitorr, the reverse reaction (reaction -3) becomes much faster than the forward reaction, and changes in water concentration will not affect measured ion abundance ratios significantly. At temperatures less than 400°K and pressures of somewhat more than 0.02 Torr, reaction 3 is very nearly at equilibrium. Yet it is in this range that step 2 proceeds essentially only in the forward direction. Equation X can therefore be modified by inclusion of all further equilibria on the assumption that they have all been achieved. Elementary considerations lead to

$$K_a = k_2[M]t / (1 + K_3[\text{H}_2\text{O}] + K_3K_4[\text{H}_2\text{O}]^2 + \dots) \quad (\text{XIV})$$

The effect on K_a and ΔH_a becomes clearer when only K_3 is considered. As the temperature is decreased, K_3 becomes larger and the denominator in (XIV) becomes greater than unity. When $K_3[\text{H}_2\text{O}] \gg 1$

$$K_a \simeq k_2[M]t / (K_3[\text{H}_2\text{O}]) \quad (\text{XV})$$

Following (XIII) and at constant $[\text{H}_2\text{O}]$

$$\Delta H_a \simeq E_2 - 2025 - \Delta H_3 \text{ cal/mol} \quad (\text{XVI})$$

Since $\Delta H_3 \simeq -18$ to -20 kcal/mol,¹² the sign of ΔH_a will eventually change. It is clear that the approach to equilibrium of reactions 3, 4, etc., will at first reduce the temperature dependence of K_a and this is indeed observed in all equilibrium studies using chemical ionization sources. Whether or not the dependence on water concentration predicted by (XV) exists at lower temperatures cannot be assessed from published data because no investigation of the effect of this parameter was reported below about 400°K .⁶

The applicability of eq X is of course a limited one and requires that $(k_2[M][\text{H}_2\text{O}] + k_{-2}[M])t$ be much less than unity. At 400°K , $k_{-2}[M]$ is entirely negligible and the exponent will meet the condition as long as the product of water pressure and time is less than 10^{-7} Torr sec and the drift gas pressure is on the order of a few Torr. This requirement does not change substantially at higher temperatures because even at 800°K the forward reaction is much faster while the residence time under otherwise identical conditions is reduced by a factor of 2 (eq XI).

Equation XIII shows clearly that data, particularly the intercept, should be weakly dependent on pressure and E/P which appears in the log term. In the limit where reaction 2 is quasi-second order, the dependence on P will vanish since E/P has normally been held constant in the earlier work. Changes in the operating conditions and the nature of the drift gas, which exerts an effect through α and μ , can readily shift values of ΔS_a by as much as 9 eu.²¹

Comparison with Experiment

Equation VIII can be tested readily at a given temperature using the data summarized in Figures 1 and 2. Insertion of the values for k_2 and K_2 given by Cunningham, *et al.*,¹² leads to the calculated curve of Figure 4; the initial slope (dotted line) is the limit of K_a/K as time goes to zero and is $[k_{-2}M]t$ according to (X). The

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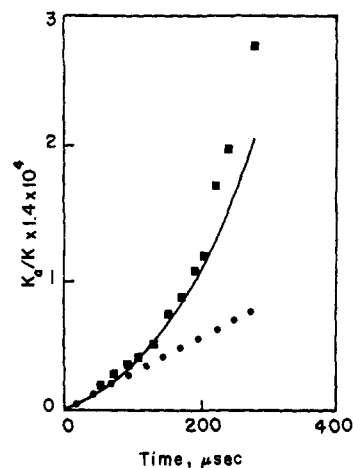


Figure 4. Experimental (points) and calculated (eq VIII, line) values of K_a/K , the ratio of the apparent to the real equilibrium constant. The slope of the line (···) is that defined by eq X for complete kinetic limitation and no reverse reaction.

agreement of calculated and experimental values of K_a/K is good at times up to about 200 μsec ; thereafter, the experimental values approach the equilibrium more rapidly than those calculated; however, it is in this range that our data are most uncertain because of low intensities. It is also possible that this change is caused by an increase in the importance of reaction 3.

Equations VIII, XI, and XIII can also be compared with measured values of ΔH reported elsewhere.^{6,11} The calculated limit (eq XIII) under complete kinetic control is $\Delta H_a = -6.9$ kcal/mol with methane as the drift gas. This is in good agreement with the value -7.0 kcal/mol reported by Beggs and Field for the same drift gas,⁶ even though experimental conditions differed somewhat from those assumed here.

It is not entirely clear why propane as the drift gas should give a substantially different value of ΔH_a .^{6,11} However, field strength in the latter work¹¹ was on the order of 23 V cm^{-1} and even at pressures of several Torr the Wannier relationship²² predicts a substantial increase in average ion energy at such values of E/P . The effect of field strength on apparent equilibrium and rate constants in simple systems will be discussed elsewhere, but it may be noted here that at low fields and written in the Wannier formulation this factor greatly affects ΔS_a but decreases ΔH_a only slightly.²³ Since energy distributions are, however, not of the simple Maxwell-Boltzmann form,^{24,25} the effect on ΔH_a of applied fields on the order of 10 V/(cm Torr) should be substantial.

Another and more probable reason for the difference in empirical values of ΔH_a may be a substantial change in the temperature dependence of reaction 2 when propane is the inert body rather than methane. However, the activation energy for this reaction has not been measured.

Conclusion

An analysis based on kinetic limitation of reactions

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demonstrates that independence of pressure and linearity of van't Hoff plots do not assure the achievement of equilibrium. It leads to a calculated value of the apparent heat of reaction which depends only on the activation energy of the clustering reaction and the functional form of the temperature dependence of mean residence times. As long as applied fields are sufficient to assure the applicability of (XI), the resultant ΔH_a will be independent of instrumental parameters, drift lengths, field strengths, etc., and will differ by approximately -2 kcal/mol from the activation energy for the forward reactions. These factors will, however, affect the intercept of van't Hoff plots and thereby exercise considerable influence on the apparent values of free energies and entropies of reaction. This is consistent with earlier observations.^{6,11}

The present considerations support the thermodynamic parameters reported by Kebarle and co-workers^{3,12,13} and DePaz, *et al.*,¹⁵ and thereby reflect on the probable structure of the hydrated proton.

Theoretical considerations,^{16,26,27} particularly the *ab initio* calculations of Newton and Ehrenson,¹⁶ are in essential agreement with these experimental thermodynamic quantities and suggest that the optimized chain structures of the lower, and chain and branched structures of the higher proton hydrates, are good representation of actual structures, that the central OH bond distance in the dihydrate is considerably greater than in H_3O^+ , and that the addition of further water molecules causes the central OH bond to shorten again gradually.

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Optical Properties of Sugars. II. Vacuum-Ultraviolet Absorption of Model Compounds

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Abstract: Vacuum-ultraviolet absorption spectra of 11 model sugar compounds were measured to 80 kK. The model sugars include three alcohols, four ethers, and four complex cyclic compounds which combine alcohol and ether chromophores. All spectra show absorption bands in the energy region 50 to 65 kK which are attributed to the presence of the oxygen atom. The spectrum due to a hemiacetal group is presented for the first time. Apparently the interaction between alcohol and ether chromophores in this group is strong so that the hemiacetal is best treated as a single chromophore. In contrast, when chromophores are separated by two carbon atoms their interactions appear weak. In this case the low-energy transitions of the simple compounds measured here are additive and can be combined to yield the spectra of the more complex molecules. The as yet unmeasured spectrum of glucose is predicted.

Sugar monomers contain a number of alcohol chromophores as well as an ether chromophore in a tetrahydrofuran or tetrahydropyran ring. These chromophores exhibit degenerate or nearly degenerate transitions so that, in order to understand the electronic transitions of a monosaccharide, it is important to assess the strength of the interactions between these groups. Such an understanding is particularly important to our laboratory since we are conducting circular dichroism studies on sugars in aqueous solution in the vacuum-ultraviolet where Cotton effects associated with at least the first band in these chromophores can be completely determined.³

It might be best to measure the electronic absorption spectra of the sugars themselves in aqueous solution for direct comparison with the circular dichroism spectra.

However, to measure spectra in aqueous solution in the vacuum uv, it is necessary to use extremely short and unknown path lengths to minimize light absorption by the solvent. Such a procedure is reasonable for circular dichroism spectra because the absorption due to the symmetric solvent cancels in the measurement, but clearly the procedure is not applicable to the measurement of absorption spectra where the path length of the sample and the blank must be identical.

As a first step we have measured the spectra of some less complex molecules which are related to sugars. Since they are measured in the vapor phase, the results are not complicated by solvent effects, but of course solvent effects must be considered if the results are generalized to aqueous solution.

The spectra of four complex model sugar compounds (tetrahydrofurfuryl alcohol, 3-hydroxytetrahydrofuran, tetrahydropyran-2-methanol, and 2-hydroxytetrahydropyran) are new in this study, as are the spectra of cyclohexanol and the cyclic ether 2-methyltetrahydropyran. The spectra of two other alcohols (methanol

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