Clustering Reactions of the Protonated Nitrogen N_2H^+ with Hydrogen Molecule in the Gas Phase

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Clustering reactions of the protonated nitrogen N_2H^+ with hydrogen molecule, $N_2H^+(H_2)_{n-1}+H_2=N_2H^+(H_2)_n$ $(n-1, n)$, were studied in a pulsed electron beam mass spectrometer with a high-pressure ion source. The values of enthalpy change $-\Delta H_{n-1,n}$(kcal/mol) and the entropy change $-\Delta S_{n-1,n}$(e.u.) obtained from the van't Hoff plots of equilibrium constants were (0, 1) 7.2, 22.6, (1, 2) 1.5, 14.0. No cluster ions larger than $N_2H^+(H_2)_2$ were observed even at −187 °C. The relatively low values of enthalpy change for the clustering reactions (0, 1) and (1, 2) suggest that the positive charge in N_2H^+ is delocalized, the N_2H^+ ion very weakly interacting with additional hydrogen molecules electrophilicly. The calculated entropy change also suggests that hydrogen molecules in $N_2H^+(H_2)_n$ are weakly bound to the core ion N_2H^+, having considerable freedom of motion in the cluster ion. The thermochemical study proves that the cluster ion $N_2H^+(H_2)_2$ does not have the structure of the protonated hydrazine $N_2H_5^+$.

Studies of ion-solvent molecule interactions in solution date back to the beginning of physical chemistry. However, it is only 10 years since a systematic study of ion-solvent molecule interactions in the gas phase was begun. Studies of ion-solvent clustering reactions in the gas phase provide direct indication of the preferred coordination of ions by solvent molecules and the energy relations between solvated species in the gas phase containing different numbers of coordinated solvent molecules.

A merit of studies in the gas phase by means of mass spectrometry is that the stoichiometry of detectable species can be deduced exactly. The mass spectrometric method also permits measurements of gas phase ion equilibria and their temperature dependence. These data in turn lead to enthalpies, entropies and free energies for ionic reactions. These thermochemical data often give information on the structure of ionic species.

A mass spectrometric study of the ions present in the air at near atmospheric pressures (≈100 Torr) led to the incidental observation[1,2] of the proton hydrates $H^+(H_2O)_n$ formed by ion-molecule reactions involving a trace of water vapor. The observation of clusters such as $NH_4^+(NH_3)_m(H_2O)_n$ and $H^+(CH_3OH)_n$ in ammonia, methanol and other gases led to the systematic study of ion-solvent molecule interactions and ion equilibria in the gas phase.[3] Because of hydrogen bonding, bond energies are very large in the water. Since the charge is very efficiently dispersed by hydrogen bonding, the relative stability difference between the favorable and the unfavorable structures is small.

Recently, Hiraoka and Kebarle investigated two clustering reactions, $H_3^+(H_2)_{n-1}+H_2=H_3^+(H_2)_n$ and $CH_5^+(CH_4)_{n-1}+CH_4=CH_5^+(CH_4)_n$.[4,5] From the thermochemical data obtained, they predicted the structure of H_3^+, CH_5^+ and of cluster ions $H_3^+(H_2)_n$ and $CH_5^+(CH_4)_n$. In both systems, the positive charge is not so well dispersed in the cluster ions as in the case of water system, because hydrogen and methane have no hydrogen bonding ability. Since the charge is not efficiently dispersed in the cluster ions, the relative stability differences between the favorable and the unfavorable structures are larger, thus making it easier to predict the structure of cluster ions.

In this investigation, the clustering reactions of the protonated nitrogen N_2H^+ with hydrogen molecule were studied. Since the protonated molecule and the solvent molecule are different, new information was expected.

Experimental

The ion-molecule reaction ion source and the mass spectrometer were described;[6] only a brief description of the procedures is given herewith.

The H_2 gas(Linde UHP) was purified by passing through a liquid nitrogen cooled trap containing molecular sieve 5 Å at atmospheric pressure. Downstream of this trap, the H_2 gas passed through a variable needle valve in order to reduce the pressure to 1—6 Torr, flowing in and out of the ion source. The H_2 gas thus prepared contains no impurities except a trace amount of nitrogen.[7]

Ionization is produced by a short pulse of 2 keV electrons which enters the sourse through a small slit (12 μm×2 mm, razor blade edges) of the field free ion source. The electron beam is pulsed "on" for 10 μs and "off" for 5 ms. Each pulse contains some 10^6 electrons. The primary ions H_2^+ and H^+ are rapidly converted by ion-molecule reactions into H_3^+. This species reacts further giving H_5^+, H_7^+, *etc.* The reaction occurs due to proton transfer from H_3^+ and H_5^+ to impurity N_2 leading to N_2H^+ and its hydrogen clusters. The vast majority of ions are ultimately destroyed by diffusion towards the wall. Some ions diffuse to the vicinity of an ion exit slit (12 μm×3 mm, razor blade edges) and escape into an evacuated region where they are accelerated, magnetically mass analyzed and detected with counting equipments attached to a multichannel analyser. Collection of some 10^4 pulses at a given m/e gave a satisfactory temporal profile of the ion with a channel dwell time of 20—30 μs.

The equilibrium constants for the clustering reactions $(n-1, n)$ were calculated by

$$K_{n-1,n} = I_n/I_{n-1} \times P_s$$

where I_n/I_{n-1} is the stationary intensity ratios of the corresponding cluster ions and P_s is the solvent (hydrogen) pressure.

Results and Discussion

General. The solvation of ions by neutral molecules is an exothermic process. Since the solvated ions may fall apart or be collisionally dissociated to reform the original reactants, it is possible that thermodynamic equilibrium can be achieved under conditions where the complex can undergo sufficient collisions to remove the heat of reaction. By the rule of thumb the achievement of equilibrium can be determined by the rate of the slow reaction, which has a rate constant $k \approx 10^{-29}$ cm^6 molecule^{-2} s^{-1}. With this value one can calculate the half-life for the clustering reaction at 3 Torr of H_2 as 2×10^{-6} s or less. The subsequent steps in the clustering sequence require considerably shorter time since their rate constants are considerably higher. Thus, thermodynamic information about the clustering reactions can be obtained from equilibrium constants. At equilibrium we have

$$-RT \ln K = \Delta G = \Delta H - T\Delta S \qquad (1)$$

The enthalpy of reaction can be obtained from the slope of a van't Hoff plot. We can evaluate ΔS if ΔG and ΔH are known.

Results. Figure 1 shows the temperature and pressure ranges for the (0, 1) equilibrium. The equilibrium constant is independent of the hydrogen pressure. Figure 2 gives the van't Hoff plots of the clustering reactions of N_2H^+ with hydrogen molecule. For the sake of comparison the results of the clustering reactions of H_3^+ with hydrogen molecule[4] are given in Fig. 2. The thermochemical values obtained are given in Table 1 together with the results of H_2 solvation reaction of HCO^+.[8] The solvent molecule is hydrogen for all the reactions.

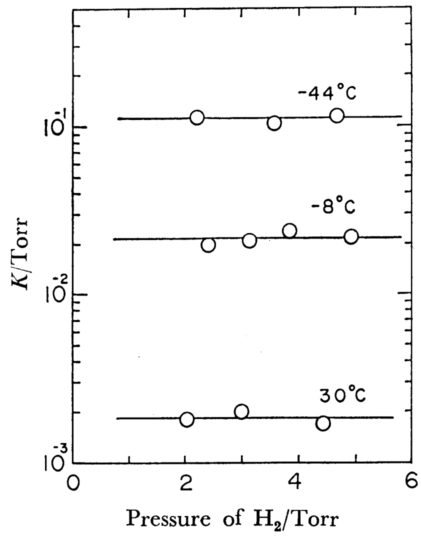

Fig. 1. Equilibrium constant $K_{0,1}$ for the reaction $N_2H^+ + H_2 = N_2H^+(H_2)$ at 3 temperatures plotted *vs.* hydrogen pressure. Standard state for K as given in these plots is 1 Torr.

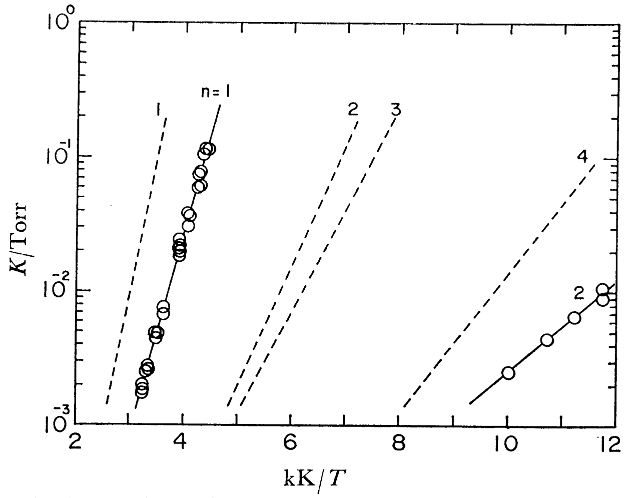

Fig. 2. van't Hoff plots for the reactions $N_2H^+(H_2)_{n-1} + H_2 = N_2H^+(H_2)_n (n-1, n)$. (----) plots for the reactions $H_3^+(H_2)_{n-1} + H_2 = H_3^+(H_2)_n$ $(n-1, n)$, Ref. 4.

Free Energy and Enthalpy Change. Decrease in $\Delta H_{n,n-1}$ $(\Delta H_{n,n-1} = -\Delta H_{n-1,n})$ with n is observed as is always the case for ion clusters. The decrease is expected because of gradual charge dispersal with the addition of new clustering molecules. The irregularity of the van't Hoff plots for the clustering reactions of H_3^+ with H_2 shown in Fig. 2 was discussed.[4] In the hydrogen experiment, cluster ions $H_3^+(H_2)_n$ for $n=1$ to 4 were observed as major ions between room temperature and -170 °C. However, in the present experiment, the ion $N_2H^+(H_2)_2$ $(n=2)$ was the largest cluster observed at low temperatures, no higher clusters $(n>2)$ being observed even at -187 °C; N_2H^+ has much lower hydrogen molecule affinity than H_3^+. The vertical distance between two adjacent van't Hoff plots taken at a constant $1/T$ corresponds to $(\Delta G_{n+1,n} - \Delta G_{n,n-1})(1/2 \cdot 3RT)$, being proportional to the free energy difference at a certain temperature T. A big gap between two van't Hoff plots thus indicates a big drop of stability

TABLE 1. THERMOCHEMICAL DATA OBTAINED FROM MEASUREMENT OF EQUILIBRIA $BH^+(H_2)_{n-1} + H_2 = BH^+(H_2)_n$ $(n-1, n)$

Reaction	$-\Delta H_{n-1,n}$[a]	$-\Delta S_{n-1,n}$[b]	$-\Delta G_{n-1,n}$[a]
(1) $N_2H^+ + H_2 = N_2H^+(H_2)$	7.2±0.2	22.6±1.0	0.4±0.4
(2) $N_2H^+(H_2) + H_2 = N_2H^+(H_2)_2$	1.5±0.3	14.0±2.0	−3.3±0.5
(3) $H_3^+ + H_2 = H_3^+(H_2)$	9.6	24.6	2.3
(4) $H_3^+(H_2) + H_2 = H_3^+(H_2)_2$	4.1	19.8	−1.8
(5) $H_3^+(H_2)_2 + H_2 = H_3^+(H_2)_3$	3.8	20.2	−2.3
(6) $H_3^+(H_2)_3 + H_2 = H_3^+(H_2)_4$	2.4	19.3	−3.4
(7) $HCO^+ + H_2 = (H_2)HCO^+$	3.9	20.5	−2.3

a) ΔH and ΔG values in kcal/mol. Standard state 1 atm. ΔG values are for 298 K. b) ΔS values in entropy units (cal/deg). Standard state 1 atm. ΔS values are for temperatures in the temperature range in which each reaction was studied.

toward dissociation of one molecule. We see from Fig. 2 that there is a very big gap between plots $n=1$ and 2 (Reactions 1 and 2, Table 1), indicating that (a) the first incoming H_2 molecule interacts with reasonable strength with N_2H^+, but the second molecule experiences very weak interactions with $N_2H^+(H_2)$, and (b) the stability of $N_2H^+(H_2)_2$ is remarkably lower than that of $H_3^+(H_2)_2$.

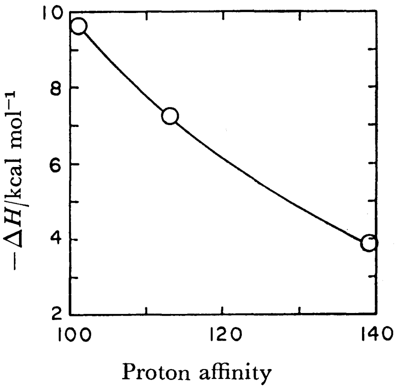

Fig. 3. Relationsflip between $-\Delta H_{0,1}$ for the reaction $BH^+ + H_2 = BH^+(H_2)$ and proton affinity for molecule B as H_2, N_2 and CO. See text.

The values of enthalpy change $\Delta H_{1,0}$ (Table 1) give the order $\Delta H(H_3^+\cdots H_2) > \Delta H(N_2H^+\cdots H_2) > \Delta H(HCO^+\cdots H_2)$, *i.e.*, the order of the hydrogen molecule affinity for each protonated species is $H_3^+ > N_2H^+ > HCO^+$. The order is opposite that of proton affinities of H_2, N_2, and CO, which are 101.0, 113.7, and 139.1 kcal/mol, respectively.[9] The relationship between proton affinities and $-\Delta H_{0,1}$ is shown in Fig. 3. For all Reactions 1, 3, and 7, the solvent molecule is hydrogen which interacts nucleophilicly with each protonated molecule. If the positive charge is more delocalized in the protonated species, the interaction of the solvent molecule with the ion should be weaker, and *vice versa*. The larger proton affinity indicates that the positive charge is more dispersed in the protonated species, and the following clustering step should be less favorable (Fig. 3). This is also the case for polar molecules which have a strong tendency to hydrogen bonding. Water has been known as the best solvent for proton. However, the proton affinity of water is the lowest among all other oxygen containing hydrocarbons.[10)

The Structure of $N_2H^+(H_2)$ and $N_2H^+(H_2)_2$. The characteristic enthalpy changes for Reactions 3—6 led to the prediction of the structure of $H_3^+(H_2)_n$.[4] For the present clustering Reactions 1 and 2, the big drop of $-\Delta H_{n-1,n}$ seems somewhat unusual. A theoretical calculation predicts that N_2H^+ has a linear equilibrium geometry.[11] However, no theoretical work has been carried out on the structure of $N_2H^+(H_2)_n$ for $n=1$. Tentatively two possible structures are suggested (Fig. 4), a solvent hydrogen molecule interacting with the terminal hydrogen atom in structure(a), and with the central nitrogen atom in structure(b). From the large electronegativity of a nitrogen atom and the relatively low proton affinity of a nitrogen molecule, an appreciable amount of positive charge is considered to be on the hydrogen atom in N_2H^+. Because of the smaller size of the hydrogen atom, the nucleophilic interaction between a solvent hydrogen molecule and the terminal hydrogen atom may be stronger than that between a solvent hydrogen molecule and the central nitrogen atom. We would like to suggest that the cluster ion(a) would be the most stable isomer of the cluster ion $N_2H^+(H_2)$. In (a), the proton is sandwiched between N_2 and H_2 molecules. In such a structure, the potential energy curve for the proton may have double potential minima.[12] Since the proton affinity of nitrogen is larger than that of hydrogen, the proton in $N_2H^+(H_2)$ should be closer to the nitrogen molecule (Fig. 4(a)).

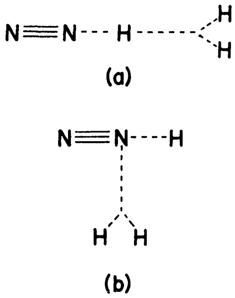

Fig. 4. Possible structures of cluster $N_2H^+(H_2)$,

When the cluster ion $N_2H^+(H_2)$ has structure(a), the second incoming hydrogen molecule would interact either with the central hydrogen atom or the nitrogen atom adjacent to the central hydrogen atom. In either case, the nucleophilic interaction would be much weaker than that for the first clustering step, since the positive charge is already dispersed in $N_2H^+(H_2)$. This might explain the big drop of the enthalpy changes for Reactions 1 and 2.

$N_2H^+(H_2)_2$ has the same chemical formula as the protonated hydrazine, $N_2H_5^+$. From a comparison of heat of formation of $N_2H^+(H_2)_2$ and $N_2H_5^+$, it can easily be shown that the cluster ion $N_2H^+(H_2)_2$ does not have the structure of protonated hydrazine. The heat of formation of $N_2H^+(H_2)_2$ can be obtained from the proton affinity of N_2 and the enthalpy changes of Reactions 1 and 2 as 244.6 kcal/mol. So far no proton affinity of hydrazine has been measured. The proton affinity of hydrazine is considered to be equal or larger than that of ammonia (202 kcal/mol) because of the inductive effect of $-NH_2$ group. Thus the heat of formation of the protonated hydrazine should be ≤ 187.8 kcal/mol. The difference between these two values is large enough to conclude that $N_2H^+(H_2)_2$ and $N_2H_5^+$ are structural isomers. Although the reaction of the formation of protonated hydrazine, $N_2H^+(H_2) + H_2 = N_2H_5^+$, is highly exothermic ($\approx 60$ kcal/mol), it must have a large free energy barrier, *i.e.*, an activation energy barrier as well as an entropy barrier, since the reaction sould undergo the rearrangement of atoms.

Entropy Change. The entropy of a molecule in the gas phase is given by

$$S = S_t + S_r + S_v + S_e \tag{2}$$

where S_t, S_r, S_v, and S_e are translational, rotational, vibrational and electronic entropy, respectively. The contribution of the electronic entropy S_e is usually negligible at normal temperatures. The translational entropy is evaluated by

$$S_t = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P - 2.315 \tag{3}$$

where R, M, T, and P are gas constant, molecular weight in atomic unit, temperature, and gas pressure in atmospheric pressure unit, respectively. The rotational entropy for a linear molecule and that for a non-linear molecule are respectively given by the equations

$$S_r = R\ln I + R\ln T - R\ln\sigma + 177.671 \tag{4}$$

$$S_r = \frac{R}{2}\ln I_A I_B I_C + \frac{3}{2}R\ln T - R\ln\sigma + 267.644 \tag{5}$$

where I and σ are the moment of inertia and the symmetry number of the molecule, respectively. The vibrational entropy is given by

$$S_v = R\sum_i\left[-\ln\left(1-\exp\left(-h\nu_i/kT\right)\right)+\frac{h\nu_i/kT}{\exp\left(-h\nu_i/kT\right)-1}\right] \tag{6}$$

where ν_i is the frequency of the i-th fundamental vibration.

The translational entropy change which is by far the most important term is readily evaluated for Reaction 1 by means of the Sackur-Tetrode equation

$$\Delta S_t = \frac{3}{2}R\ln\frac{M_3}{M_1\cdot M_2} - \frac{5}{2}R\ln T + R\ln P + 2.315 \tag{7}$$

where M_1, M_2, and M_3 are the molecular weights of N_2H^+, H_2, and $N_2H^+(H_2)$, respectively. Substituting 265 K for T, we obtain $\Delta S_t = -27.3$ e.u. The temperature 265 K corresponds to the average in the temperature range of the van't Hoff plot from which $\Delta H_{0,1}$ and also $\Delta S_{0,1}$ were obtained (Fig. 2).

In order to evaluate the rotational entropy change, we should know the structure of N_2H^+ and $N_2H^+(H_2)$. The linear structure of N_2H^{+}[11] theoretically predicted leads to the moment of inertia of $N{\equiv}N\cdots H^+$ of 1.74×10^{-39} g·cm². The following assumptions will be made for the possible structures of $N_2H^+(H_2)$ shown in Fig. 4. Since the $N_2H^+\cdots H_2$ ion consists of weakly bonded N_2H^+ and H_2, the vibrational modes in H_2 and N_2H^+ would be essentially preserved in $N_2H^+\cdots H_2$. The distance between H atom and H_2 in structure(a), and N atom and H_2 in structure(b) is 1.9 Å. This value is adopted on the basis of the theoretical calculation done by Yamabe, Hirao and Kitaura.[13] They predicted the bond distance $H_3^+\cdots H_2$ of 1.857 Å. Since the bond energy of $H_3^+\cdots H_2$ (9.6 kcal/mol) is of the same order as that of $N_2H^+\cdots H_2$ (7.2 kcal/mol), the predicted value would not be in large error. Actually, the calculated rotational entropy changes are rather insensitive to a small change in the molecular structure. Substitution of these values in Eqs. 4 and 5 leads to $\Delta S_r = 1.3$ e.u. for the cluster ion(a) and $\Delta S_r = 4.2$ e.u. for the cluster ion(b). The total entropy change $\Delta S_{0,1}$ experimentally determined is -22.6 e.u., indicating that $\Delta S_v \approx 3$ e.u. for the formation of the cluster ion(a) and $\Delta S_v \approx 1$ e.u. for that of the cluster ion(b). The new vibrational modes in $N_2H^+(H_2)$ can be represented by a rocking motion with ω_1 in which alternately one end of H_2 and then the other swings toward N_2H^+, a nearly free internal rotation with ω_2 of H_2 around the bond $N_2H^+\cdots H_2$, a bond stretching vibration ω_3, and two normal bending vibrations ω_4 and ω_5. Salmon and Poshusta[14] have estimated $\omega_1 \approx \omega_2 \approx 200$ cm^{-1} and $\omega_4 \approx \omega_5 \approx 50$ cm^{-1} for $H_3^+\cdots H_2$. Frequencies of 50 and 200 cm^{-1} lead to vibrational entropy changes of -1.8 and -2.44 e.u. at 265 K, respectively. If the values are used for vibrations in $N_2H^+\cdots H_2$, the four vibrations lead to $\Delta S_v = -8.5$ e.u. Evidently the actual vibrations in $N_2H^+\cdots H_2$ should be considerably milder than the predicted vibrations in $H_3^+\cdots H_2$. Certain vibrations with the frequency of 30 cm^{-1} ($\Delta S_v \approx 1.6$ e.u) or less and the near free internal rotation of H_2($\Delta S_v \approx 2$ e.u.) should be taken into consideration in order to explain the estimated ΔS_v.

A number of assumptions would be required for the evaluation of the entropy change for Reaction 2. The translational entropy change $\Delta S_{1,2}$ calculated by Eq. 7 is -21.9 e.u. at 90 K. The temperature 90 K corresponds to the average in the temperature range of the van't Hoff plot for Reaction 2. The total entropy change $\Delta S_{1,2}$ experimentally determined is -14.0 e.u., indicating that $\Delta S_r + \Delta S_v = 7.9$ e.u. We obtain $\Delta S_r \approx 1$ e.u. by assuming several structures of $N_2H^+(H_2)_2$ in which an additional hydrogen molecule interacts with clusters(a) and (b) with the bond length of 2 Å. This value leads to the value of 7 e.u. for ΔS_v. The large positive value of the predicted vibrational entropy change strongly suggests that bonds in $N_2H^+(H_2)_2$ are very loose, additional hydrogen molecules having a large freedom of motion in the cluster ion.

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