Reversible Reactions of Gaseous Ions.
VII. The Hydrogen System

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Abstract: The equilibrium $H_3^+ + H_2 \rightleftarrows H_5^+$ has been studied at pressures up to 8 Torr of hydrogen over the temperature range +159 to −26°. The thermodynamic results obtained are: $K_{300} = 31$; $\Delta G°_{300} = -2.0$ kcal/mol; $\Delta H° = -9.7$ kcal/mol; and $\Delta S° = -25.5$ eu. The equilibrium $H_5^+ + H_2 \rightleftarrows H_7^+$ has been studied over the temperature range −134 to −171° and gave the results: $K_{300} = 0.09$; $\Delta G°_{300} = +1.4$ kcal/mol; $\Delta H° = -1.8$ kcal/mol; $\Delta S° = -10.8$ eu.

Mobility studies[1] suggest that H_5^+ has a small binding energy relative to H_3^+ and H_2. Several theoretical studies of H_5^+ have been reported. *Ab initio* calculations by Poshusta and coworkers[2,3] predicted an elongated tetrahedral geometry resembling two H_2 molecules bound together by a central proton. A binding energy of 10.8 kcal/mol was found.[3] Easterfield and Linnett[4] used a molecular obital approach and found the most stable structure to be more like a $H_3^+ \cdots H_2$ complex in which the H_2 is perpendicular to the H_3^+ plane and to a line extending from the midpoint of the base of the H_3^+ triangle, through the H_3^+ apex and through the H_2 midpoint. The binding energy relative to H_3^+ and H_2 was calculated to be 9 kcal/mol. Kaplan and Rodimova[5] have used a valence-bond method and found a very high value of 92 kcal/mol for the distorted tetrahedral geometry. Huang, Schwartz, and Pfeiffer[6] used a SCF molecular orbital model and found an $H_3^+ \cdots H_2$ geometry for H_5^+ similar to that of Easterfield and Linnett, and a binding energy of 4.25 kcal/mol. Quantitative theoretical studies of hydrogen systems larger than H_5^+ have not been reported. An experimental value of $\Delta H = -5.1 \pm 0.6$ kcal/mol has been reported by Arifov, *et al.*,[7,8] for the reaction $H_3^+ + H_2 \rightleftarrows H_5^+$ from a mass spectrometric kinetic study at 10 to 40 Torr hydrogen pressure over the temperature range 7 to 42°. They were unsuccessful in detecting ions H_n^+ with n greater than 5. Clampitt and Gowland[9] obtained ion clusters H_n^+ with n as large as 99 by low energy electron bombardment of solid hydrogen at −271°. They found that, except for H_2^+, n is odd for all ions and suggested that these ions are formed by the clustering of H_2 molecules around an H_3^+ nucleus.

In this paper we report results of high pressure mass spectrometric studies of the equilibria

$$H_3^+ + H_2 \rightleftharpoons H_5^+ \qquad (1)$$

$$H_5^+ + H_2 \rightleftharpoons H_7^+ \qquad (2)$$

Experimental Section

In order to operate the Esso Chemical Physics mass spectrometer at higher reactant pressures, two modifications were made. The existing ion source diffusion pump was replaced with a Norton Vacuum VHS-4 pump which has a pumping speed of 1200 l./sec. The electron acceleration energy was made variable from 220 to 600 V, rather than a fixed 220 V. The latter modification increased the penetration of the electrons into the ionization chamber which was required in order to have sufficient ion intensity at higher source pressures. With these modifications, the instrument could be operated at source pressures up to 8 Torr of hydrogen.

The remainder of the apparatus and technique have been described in previous papers.[10,11] The mass spectrometer was equipped with the ion source designated previously as source III, which can be heated to 300° and cooled to approximately liquid nitrogen temperature. A 200 line per inch wire screen (maintained at focus electrode potential) is located between the focus electrode and the analyzer entrance slit, and the distance between this screen and the ion exit slit of the source is relatively large (12 mm). Thus one is assured that little or no penetration of the ion acceleration voltage (3000 V) into the source region occurs. The repeller and the focus electrodes were maintained at minimum operating potentials (3-V repeller and 4-V focus) needed to achieve a usable sensitivity. The electron collector electrode and the electrode in the electron gun immediately in front of the ionization chamber were both maintained at ionization chamber potential. These are the conditions previously referred to as approximate field-free conditions, and with them the ions in the ionization chamber and downstream of the ion exit slit for a distance of 12 mm are subjected to the weakest electric fields compatible with attaining an adequate sensitivity of the equipment. Our experience has been that the occurrence of collision-induced dissociations in the ion gun is manifested by distortions of the peak shape of the ion produced by the dissociation, and consequently the shapes of the various peaks of importance were kept under continuous surveillance during the course of the work. No distortion of the peak shapes were observed.

The electron collimating magnet was operated at the lowest field in order to minimize mass discrimination.

Matheson Ultra High Purity hydrogen (analysis stated as N_2 <1 ppm, O_2 1 ppm, He 50 ppm) was used. Traces of water in the hydrogen were significantly reduced in magnitude by passing the hydrogen through a coil submersed in liquid nitrogen.

Results

A. The Equilibrium $H_3^+ + H_2 \rightleftarrows H_5^+$. The mass spectra obtained at four different temperatures for the above system are shown in Table I. In addition to the ions of interest there are ions due to the impurities oxygen, water, and nitrogen. The latter two are the major contaminants and their effect on the 3,5-equilibrium constant will be discussed later. The metastable ion observed at $m^* = 27.1$ has been assigned to the decomposition $N_2H_3^+ \rightarrow N_2H^+ + H_2$.

If the ion H_5^+ is produced by reversible reaction 1,

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Table I. Mass Spectra of Hydrogen above Room Temperature[a]

		Relative intensity $I_i/\Sigma I_i$ at			
m/e	Ion	112°	87°	75°	38°
3	H_3^+	0.428	0.354	0.344	0.294
5	H_5^+	0.00076	0.0018	0.0028	0.013
17	OH^+	0.0061	0.0066	0.0086	0.0057
18	H_2O^+	0.00040	0.00048	0.00067	0.00072
19	H_3O^+	0.0356	0.0308	0.0552	0.0960
$m^* = 27.1$		0.00075	0.00072	0.0013	0.0012
29	N_2H^+	0.524	0.601	0.582	0.588
30	$N_2H_2^+$	0.0023	0.0023	0.0030	0.0028
31	$N_2H_3^+$	0.00046	0.00070	0.00097	0.0031
32	O_2^+	0.00096	0.00114	0.0013	0.0011
45	$N_3H_3^+$, N_2OH^+	0.00056	0.00086	0.00097	0.0013

[a] $P_{H_2} = 5.2$ Torr.

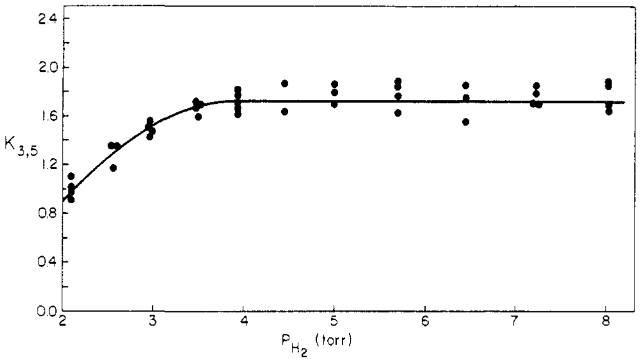

Figure 1. Equilibrium constant *vs.* H_2 pressure for $H_3^+ + H_2 \rightleftharpoons H_5^+$, $T = 59°$.

and the reaction is assumed to have achieved equilibrium we may write an equilibrium constant for the reaction.

$$K_{3,5} = \frac{I_5}{I_3}\frac{1}{P_{H_2}} \tag{3}$$

This constant should be independent of the pressure of hydrogen. Figure 1 illustrates the effect of varying the pressure of hydrogen on the value of $K_{3,5}$, and one sees that the value of the equilibrium constant rises as the pressure is increased to about 3.5 Torr and then is constant up to about 8 Torr, which was the upper limit of pressure at which the mass spectrometer could be operated. This behavior is that to be expected for a reversible reaction which achieves equilibrium above some minimum pressure. It should be kept in mind that in this system the hydrogen acts both as a reactant and a third body. Our past experience with methane[11-14] and propane[15,16] has been that reversible reactions in the mass spectrometer achieve equilibrium at third body pressures of approximately 1 Torr. That we must employ higher pressures in the case of hydrogen is probably a consequence of the shorter ion-residence times and the lower efficiency of hydrogen in absorbing the exothermic heats of reaction.

In the quantitative experiments the repeller was maintained at a potential of 3 V, which is a compromise between the zero voltage desirable for thermodynamic reasons and the finite repeller needed with our machine to obtain a usable sensitivity. The effect of the repeller voltage (varied from 1 to 10 V) upon $K_{3,5}$ was investigated at 5.2 Torr of hydrogen pressure at temperatures of 59 and 124°. In both cases $K_{3,5}$ decreased linearly from 1 to 3 V repeller and then slowly levelled off at higher voltages. The extrapolated value of the equilibrium constant at zero volts repeller was found to be a factor of 2.8 times larger than the value obtained at 3 V at both temperatures.

The magnitude of $K_{3,5}$ was found to be independent of the electron acceleration voltage from 220 to 600 V.

The effect of the presence of H_2O on $K_{3,5}$ was investigated. The addition of water corresponding to a source pressure of 0.0008 Torr to hydrogen at 5.2 Torr pressure at 59° caused the *m/e* 19 intensity to increase 20-fold, but produced virtually no change in the 3+ and 5+ intensities, and hence no change in $K_{3,5}$. It was also found that the *m/e* 29 intensity decreased 40-fold due to the reaction

$$N_2H^+ + H_2O \longrightarrow H_3O^+ + N_2$$

The effect of added nitrogen on $K_{3,5}$ was investigated at 5.2 Torr of hydrogen at 50°. $K_{3,5}$ was found to be independent of nitrogen pressure. At the highest nitrogen pressures used ($P_{N_2} = 0.035$ Torr) the intensity of both H_3^+ and H_5^+ decreased tenfold, and the *m/e* 29 to *m/e* 3 intensity ratio increased to 45 to 1. This amount of nitrogen is well above that present in the ultra high purity hydrogen, as evidenced by an *m/e* 29 to *m/e* 3 intensity ratio of about 2 to 1 (see Table I). Thus, since the magnitude of the 3,5 equilibrium constant was independent of the water and nitrogen pressures, it was deemed unnecessary to attempt to remove the last traces of these impurities.

The values of $K_{3,5}$ (eq 3) were determined as a function of the temperature of the ion source at hydrogen pressures of about 5.2 Torr. Since the hydrogen pressure in the ion source varies somewhat with the temperature of the source, slight changes in the controls determining the hydrogen flow were made over the course of the experiment in order to maintain the pressure at about 5.2 Torr. The value of the hydrogen pressure used in the equilibrium constant expression (3) was always the value determined experimentally at the temperature in question. Duplicate experiments involving measuring the spectra over the temperature range +159 to −26° were made on separate days, and excellent agreement between the experiments was obtained.

A van't Hoff plot for $K_{3,5}$ is given in Figure 2. The plot is linear from 159 down to 38°. The nonlinear

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(16) S. L. Bennett and F. H. Field, *ibid.*, **94**, 5186 (1972).

Table II. Experimental Thermodynamic Quantities for Equilibrium Reactions

Equilibrium	K_{300}[a]	ΔG°_{300}, kcal/mol	ΔH°, kcal/mol	ΔS°, eu
$H_3^+ + H_2 \rightleftarrows H_5^+$[b]	18.6	−1.74	−5.1	−11.2
$H_3^+ + H_2 \rightleftarrows H_5^+$[c]	31	−2.0	−9.7	−25.5
$H_5^+ + H_2 \rightleftarrows H^{7+}$[c]	0.09	+1.4	−1.8	−10.8

[a] Standard state = 1 atm. [b] Arifov, *et al.*, ref 7 and 8. [c] Present data.

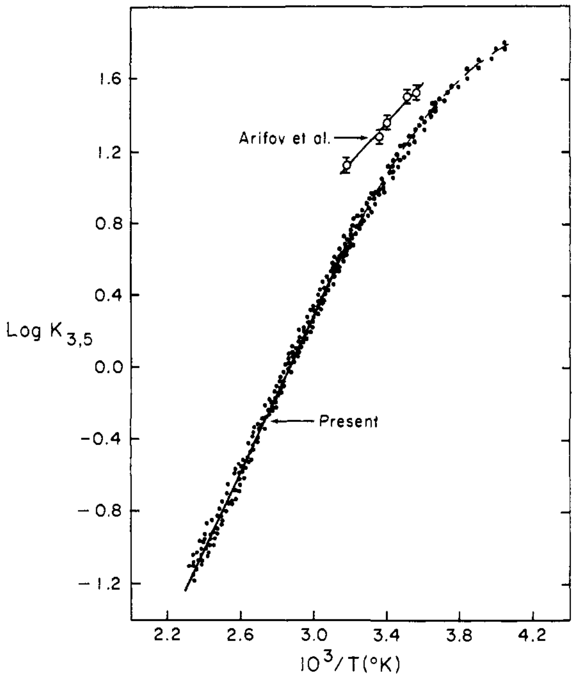

Figure 2. van't Hoff plot for $H_3^+ + H_2 \rightleftarrows H_5^+$. Closed circles, present data, P_{H_2} = 5.2 Torr. Open circles, Arifov, *et al.*, ref 7 and 8. Standard state = 1 atm.

behavior at low temperatures is a phenomenon which has generally been encountered in our mass spectrometric equilibrium studies. From our mathematical analysis[15] of these systems, we believe that the explanation for the curvature in the van't Hoff plots results from the time limitations on the establishment of equilibrium in the ionization chamber of the mass spectrometer. The behavior predicted by the calculations has been observed in this system; namely, the nonlinear behavior sets in when the product to reactant ion ratio is greater than 5%. Also shown in Figure 2 are the results of Arifov, *et al.*, constructed from the data in ref 7 and 8.

Thermodynamic quantities have been obtained from least squares fits of the linear portions of the van't Hoff plots. The average thermodynamic values obtained were K_{300} = 10.3 ± 0.3, ΔG°_{300} = −1.39 ± 0.02 kcal/mol, ΔH° = −9.7 ± 0.2 kcal/mol, and ΔS° = −27.7 ± 0.6 eu. The limits of error are the deviation from average of the duplicate experiments. Since operating the repeller at 3 V lowers the absolute magnitude of $K_{3,5}$ by a factor of 2.8, but has no effect upon the temperature dependence of the equilibrium constant, the above values of K_{300}, ΔG°_{300}, and ΔS° have been adjusted accordingly to give the thermodynamic values extrapolated to zero repeller voltage. These values are given in Table II. The values of Arifov, *et al.*, are also shown.

Table III. Mass Spectra of Hydrogen at Low Temperatures[a]

m/e	Ion	Relative intensity $I_i/\Sigma I_i$ at: −132°		−153°	−162°	−171
3	H_3^+	0.302		0.363	0.381	0.376
5	H_5^+	0.162	w	0.157	0.167	0.180
7	H_7^+			0.00245	0.00503	0.00890
*m** = 14.8		0.00211		0.00254	0.00236	0.00213
17	OH^+	0.00125		0.00106	0.00121	0.00087
19	H_3O^+	0.00123		0.00117	0.00080	0.00086
*m** = 27.1		0.0211		0.0265	0.0240	0.0212
29	N_2H^+	0.115		0.0927	0.0876	0.0798
30	$N_2H_2^+$	0.00206		0.00145	0.00172	0.00156
31	$N_2H_3^+$	0.218		0.185	0.176	0.165
32	O_2^+	0.00693		0.00874	0.00735	0.00615
35	$O_2 \cdot H_3^+$	0.0888		0.0802	0.0720	0.0741
45	$N_3H_3^+$	0.00110		0.00081		
57	N_4H^+	0.0573		0.0569	0.0513	0.0608
58	$N_4H_2^+$				0.00156	0.00152
61	$N_4H_5^+$	0.0169		0.0170	0.0188	0.0182
65	$N_4H_9^+$	0.00215		0.00314	0.00207	0.00211

[a] P_{H_2} = 4.3 Torr.

B. The Equilibrium $H_5^+ + H_2 \rightleftarrows H_7^+$. The mass spectra obtained at four different temperatures for the above system are shown in Table III. The ion H_7^+ does not appear in the spectrum until the source temperature is reduced to −134°. Again the impurity ions are those derivable from traces of H_2O, O_2, and N_2. The metastable ion observed at *m** = 14.8 has been assigned to the decomposition $N_4H^+ \rightarrow N_2H^+ + N_2$.

Values of the equilibrium constant, $K_{5,7}$, for reversible reaction 2 were determined as a function of temperature at hydrogen pressures of about 4.3 Torr. Since a pressure of 4.3 Torr at these temperatures is roughly equivalent, in terms of particle density, to 8 Torr at room temperature, we feel confident in assuming that equilibrium is established for this reaction. Duplicate measurements were made on separate days and excellent agreement was obtained.

A van't Hoff plot is given in Figure 3. The average thermodynamic values obtained from the van't Hoff plot were K_{300} = 0.03 ± 0.3, ΔG°_{300} = +2.14 ± 0.17 kcal/mol, ΔH° = −1.8 ± 0.1 kcal/mol, and ΔS° =

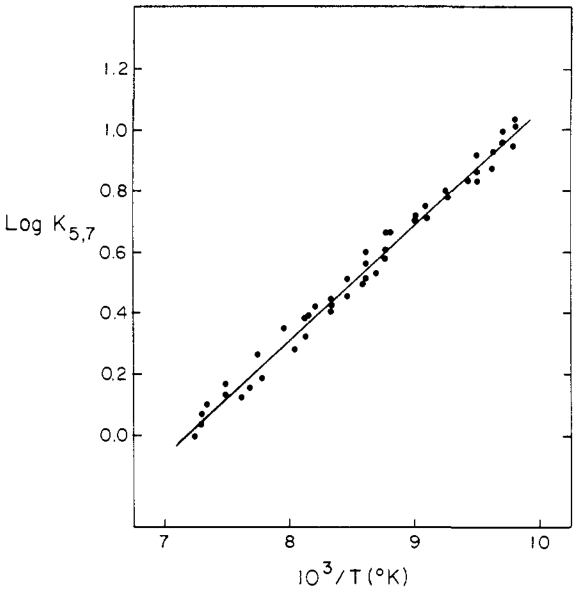

Figure 3. van't Hoff plot for $H_5^+ + H_2 \rightleftarrows H_7^+$. Standard state = 1 atm. P_{H_2} = 4.3 Torr.

−13.1 ± 0.9 eu. The values extrapolated to zero repeller voltage are given in Table II. Nonlinear behavior is not observed here since at the lowest temperature attainable (−171°) the product to reactant ion ratio has just reached 5%.

Discussion

Although it is encouraging that there is good agreement in the absolute magnitude of $K_{3,5}$ between the present results and those of Arifov, *et al.*, their $\Delta H°$ and $\Delta S°$ values do not agree well with ours. Although impure hydrogen was employed by Arifov, *et al.*, judging by the presence of copious quantities of N_2H^+ and H_3O^+ plus higher hydrates (see table in ref 8), the important fact to be observed is that their 3,5-equilibrium constant has been measured over a very narrow temperature range. Furthermore, the temperature range over which their data were obtained corresponds to the nonlinear region of our data. Their H_5^+ to H_3^+ intensity ratio was 1.1 at 40 Torr and room temperature.[8] Our experience has been that nonlinear behavior sets in when the product to reactant ratio is greater than approximately 0.1. Hence we suspect the data of Arifov, *et al.*, are not at equilibrium, and that their measurements could have profitably been extended to higher temperatures.

The association ion H_7^+ is indeed weakly bound. This is experimentally manifested in the fact that it does not appear in the spectrum at temperatures above about −135°, The entropy change for the 5,7 reaction is somewhat more positive than that for the 3,5-reaction, and is due probably to the lower binding energy of H_7^+ and its weaker, low frequency vibrational modes relative to H_5^+.

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Kinetics of Disproportionation of Radical Anions of Tetraphenylethylene Induced by Flash Photolysis. Effect of Ionic Aggregations on the Rate of Disproportionation

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Abstract: Flash photolysis of an equilibrium mixture of tetraphenylethylene (T) and of sodium salts of its radical anion ($T\cdot^-$) and dianion (T^{2-}) leads to ejection of electrons from T^{2-} followed by their capture by T. Thus, the equilibrium is upset, the concentration of $T\cdot^-$ increases and that of T and T^{2-} decreases. In the dark period following the flash the system returns to equilibrium. The kinetics of this relaxation was investigated. It was found that the equilibrium is reestablished by reaction 2, ($T\cdot^- + T\cdot^-,Na^+ \rightleftarrows T + T^{2-},Na^+$) $k_2 = 10 \times 10^6\ M^{-1}\ sec^{-1}$ and $k_{-2} = 3 \times 10^6\ M^{-1}\ sec^{-1}$. Rates of reactions 1 ($2T\cdot^-,Na^+ \rightleftarrows T + T^{2-},2Na^+$) and 3 ($2T^- \rightleftarrows T + T^{2-}$) are too slow to contribute significantly to the rate of the observed process. The equilibria 1 and 3 are reestablished through rapid dissociation–associations of ionic species, *e.g.*, $T\cdot^-,Na^+ \rightleftarrows T\cdot^- + Na^+$ and $T^{2-},2Na^+ \rightleftarrows T^{2-},Na^+ + Na^+$, which accompany reaction 2.

Disproportionation of radical anions of tetraphenylethylene (T) was studied by several research groups[1,2] who focussed their interest on the equilibrium established in the system $2T\cdot^- \rightleftarrows T^{2-} + T$ ($T\cdot^-$ and T^{2-} denote the radical anion and the dianion of T, respectively). In most solvents used in such studies the anions and dianions are paired, at least partially, with the cations and therefore it is necessary to differentiate among the individual equilibria, *e.g.*,

$$2T\cdot^-,Na^+ \rightleftarrows T^{2-},2Na^+ + T \qquad K_1$$

$$T\cdot^-,Na^+ + T^-\cdot \rightleftarrows T^{2-},Na^+ + T \qquad K_2$$

$$2T\cdot^- \rightleftarrows T^{2-} + T \qquad K_3$$

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