is relatively unproblematic. As all motions are in the fast limit on the deuterium time scale, the two observed lines are very narrow, so that obtaining spectra with good signal-to-noise ratio presents no problems. For lipids in the liquid-crystalline phase it is thus even possible to perform more time-consuming pulse experiments, which are for instance necessary to determine the relaxation times T_{1Z} and T_{1Q} .^{22,27,38}

More difficult is the recording of spectra of lipids in the gel phase due to the great width of the spectra and the low signalto-noise ratios encountered. However, we succeeded in recording gel-phase spectra of oriented DPPC and DMPE.

In the case of oriented DPPC we could not simulate the experimental spectra, due to the complexity of the system. Tilting of chains, reorientational correlation times close to the intermediate exchange regime, and undulations of the bilayer surface leading to very complex distribution functions for the director precluded successful line-shape simulations. Additional 2D ²H NMR spectra of powder samples in combination with T_{1Z} and T_{2e} experiments on oriented systems could probably resolve the question, whether the previously used models for describing reorientational motions in gel-phase PC bilayers are correct.

For DMPE angular-dependent spectra of the gel phase could be recorded with relatively good quality. After spectral subtraction of powder patterns originating from unoriented material, we succeeded in simulating the spectra with a simple six-site jump model used previously for the simulations of powder patterns of lipids in the gel phase. Agreement between simulated and experimental spectra could be improved when a Gaussian distribution of director axes was included. This indicates that the bilayers of oriented lipids in the gel state are distorted by surface undulations.

With this paper we could show that despite experimental problems it is possible to obtain spectra of oriented lipids in the gel phase. This method can thus offer an alternative to other difficult and time-consuming methods, such as relaxation time measurements or 2D experiments, though a successful interpretation of the observed spectra is possible only when the reorientational motions are not of too great complexity.

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Ion Chemistry at High Temperatures. 1. Thermochemistry of the Ammonium Ion from Variable-Temperature Equilibrium Measurements. Proton Transfer, Association, and Decomposition Reactions in Ammonia, Isobutene, and *tert*-Butylamine

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At 580-680 K, the proton-transfer reaction $t-C_4H_9^+ + NH_3 \leftrightarrow NH_4^+ + i-C_4H_8$ is in equilibrium in mixtures containing ammonia and isobutene. In the same mixtures, $t-C_4H_9NH_3^+$ is also formed reversibly, and kinetic experiments identify the addition/thermal decomposition equilibrium $NH_4^+ + i-C_4H_8 + M \leftrightarrow t-C_4H_9NH_3^+ + M$. The decomposition of $t-C_4H_9NH_3^+$ is at the low-pressure limit, with rate constants of $(1-14) \times 10^{-14}$ cm³/s, and $E_a = 29.1$ kcal/mol. The thermally activated addition of NH_4^+ to $i-C_4H_8$ shows third-order kinetics with $k = (2-6) \times 10^{-29}$ cm⁶/s and a negative temperature coefficient of $k = AT^{-10.8}$. Equilibrium studies of the proton-transfer reaction yield $\Delta H^\circ = -12.5$ kcal/mol and $\Delta S^\circ = -6.1$ cal/(mol K). Referred to PA($i-C_4H_8$) = 195.9 kcal/mol, these results yield PA(NH_3) = 208.4 kcal/mol, at the high end of published values ranging from 202 to 210 kcal/mol (PA = proton affinity). For the addition reaction, the equilibrium studies yield $\Delta H^\circ = -34.9$ kcal/mol and $\Delta S^\circ = -39.2$ cal/(mol K). These results lead to PA($t-C_4H_9NH_2$) = 228.7 kcal/mol, compared with the recommended value of 221 kcal/mol.

Introduction

The relative proton affinities (PA's) of hundreds of molecules have been measured and compiled.¹ Most measurements reported to date were obtained from equilibrium (1) measured at a single temperature (<350 K).

$$AH^+ + B \leftrightarrow BH^+ + A \tag{1}$$

Relative proton affinities are defined by ΔH°_{1} , and ΔS°_{1} must be calculated or estimated to derive ΔH°_{1} values from the measured ΔG°_{1} . However, for most ions the spectroscopic information required to calculate ΔS°_{1} is not available, and it is preferable that ΔH°_{1} is derived from the temperature dependence of ΔG°_{1} .

Among the proton affinities tabulated, ammonia takes a special place since it is frequently used as a reference standard. However, values for $PA(NH_3)$ have fluctuated over the past 20 years between 202 and 210 kcal/mol, due in part to the experimental difficulties involved in using ammonia, which absorbs strongly

on surfaces and creates difficulties in pressure measurement.

In the present work we use the proton affinity of $i-C_4H_8$ as a standard to measure PA(NH₃). Isobutene is a useful reference compound since the ΔH_f° of its protonated form, $t-C_4H_9^+$, has been obtained from threshold measurements with a reported accuracy of ± 1 kcal/mol.¹ Using pulsed high-pressure mass spectrometry, equilibrium (1) can be directly measured when A = $i-C_4H_8$ and B = NH₃, and the temperature dependence of $\ln K_1 vs 1/T$ yields ΔH° directly. Therefore, neither the absolute pressure of NH₃ nor ΔS°_1 is required to obtain the relative PA's.

In NH₃-*i*-C₄H₈ mixtures, we also found that the adduct ion t-C₄H₉NH₃⁺ was formed and was in equilibrium with t-C₄H₉⁺ and NH₄⁺ at 300-400 °C, participating in a complex reaction cycle. We shall identify the pertinent reactions and report some kinetic parameters. Data on the thermochemistry of NH₄⁺ and t-C₄H₉NH₃⁺ from variable-temperature equilibrium measurements are also presented.

Experimental Section

Measurements were taken with the NIST pulsed high-pressure mass spectrometer using standard procedures.²⁻⁴ Gas mixtures

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Figure 1. Time-resolved normalized ion intensities in a mixture of 0.0024% NH₃, 10% C(CH₃)₄, and 90% CH₄ at 544 K, total pressure 2.65 Torr. The plots show that $t-C_4H_9^+$ protonates NH₃ with negligible association. Data shown after termination of 1-ms electron pulse.

were ionized by 1-ms pulses of 500-1000-eV electrons, and ion signals were followed to reaction times of 2-4 ms. Reaction mixtures contained 0.001-1% NH₃, i-C₄H₈, or t-C₄H₉NH₂ in CH₄ with a trace of CHCl₃ added as electron capture agent to increase ion residence times. In some experiments, small quantities of C_6H_6 were added as a chemical ionization moderator to generate $C_6H_7^+$ rather than the more exothermic CH_5^+ and $C_2H_5^+$ protonating agents. In other experiments C(CH₃)₄ was also added as a source of $t-C_4H_9^+$ ions.

The NIST temperature measurement and ion detection systems were recalibrated recently as described elsewhere.⁴ These and other possible sources of error are discussed below.

Results and Discussion

The reactions of interest are reactions 2-4 in the forward and reverse directions.

$$t - C_4 H_9^+ + NH_3 \rightarrow NH_4^+ + i - C_4 H_8$$
⁽²⁾

$$NH_4^+ + i - C_4 H_8 \rightarrow t - C_4 H_9 NH_3^+$$
 (3)

$$t - C_4 H_9^+ + N H_3 \rightarrow t - C_4 H_9 N H_3^+$$
(4)

We shall identify the reactions that are significant under the present conditions and present evidence for the occurrence of the decomposition reaction -3 and the reverse activated condensation reaction 3. The data will confirm the absence of (4) and (-4)as significant channels under our conditions and reveal other minor decomposition channels of $t-C_4H_9NH_3^+$. In addition to presenting quantitative kinetic data on reactions 3 and -3, equilibrium (2) will be used to obtain $PA(NH_3)$ and equilibrium (3) to obtain $\Delta H^{\circ}_{f}(t-C_{4}H_{9}NH_{3}^{+})$, and from that $PA(t-C_{4}H_{9}NH_{2})$.

Reaction between $t-C_4H_9^+$ and NH_3 . This reaction, i.e., reaction 2, is an exothermic and exergonic ion-molecule proton-transfer reaction, which usually proceed at the ion-molecule capture collision rate. The rate constant k_2 has been measured by several groups at 300 K as $(0.9-1.9) \times 10^{-9}$ cm³/s,⁵ compared with the calculated capture rate of 2.1×10^{-9} cm³/s.⁶ The t-C₄H₉⁺ + NH₃ system also showed an association channel, i.e., reaction 4 at 200-450 K. However, the contribution was only 2.5% of the total rate and was independent of temperature.⁷ We examined this reaction in a mixture of 10% C(CH₃)₄ and 0.0069% NH₃ in methane, where the initial chemical ionization creates mainly $t-C_4H_9^+$. The variation of ion concentrations with time is shown in Figure 1, and it is clear that the condensation channel (3) is insignificant under these conditions. In agreement with previous



Figure 2. Time-resolved normalized ion intensities in a mixture of 0.0034% t-C₄H₉NH₂ in CH₄ at 676 K, total pressure 3.05 Torr. The plots show that t-C₄H₉NH₃⁺ decomposes mainly to form NH₄⁺, which regenerates $C_4H_9NH_3^+$ by proton transfer, resulting in a steayd-state cycle.



Figure 3. Second-order rate constant k_{-3} for $t-C_4H_9NH_3^+ \rightarrow NH_4^+ +$ $i-C_4H_8$ obtained according to eq 6 from steady-state concentrations in mixtures of 0.0034% t-C4H9NH2 in CH4 or 0.0044% t-C4H9NH2 plus 0.034% C₆H₆ (as a proton-transfer moderator) in CH₄ at 676 K. Data show that decomposition is at low-pressure limit as the second-order rate constant is independent of pressure.

results, it amounts to <3% of the total ion chemistry. We obtain $k_2 = 1.5 \times 10^{-9} \text{ cm}^3/\text{s}$, which is comparable to the calculated capture rate constant of 1.7×10^9 cm³/s at 600 K. A similar value for k_2 was obtained in the *i*-C₄H₈ + NH₃ reaction system as discussed below.

Decomposition of $t-C_4H_9NH_3^+$. The decomposition of t- $C_4H_9NH_3^+$ was studied in reaction mixtures containing t- $C_4H_9NH_2$ in methane. A small amount (0.03 mol %) of C_6H_6 was added to generate $C_6H_7^+$ as a moderate protonating agent in order to minimize the initial fragmentation of $t-C_4H_9NH_3^+$ induced by highly exothermic proton transfer from CH₅⁺ and $C_2H_5^+$. Ion profiles found in this reaction system are shown in Figure 2, and it is apparent that the thermal decomposition of $t-C_4H_9NH_3^+$ creates mostly NH_4^+ . The minor ion $C_4H_7NH_3^+$ is also observed, possibly resulting from protonation of C₄H₇NH₂ produced by heterogeneous pyrolysis. The ammonium ion then regenerates $t-C_4H_9NH_3^+$ via reaction 5, resulting in a cycle of reactions -3 and 5 which reach steady state.

$$NH_4^+ + t - C_4H_9NH_2 \rightarrow t - C_4H_9NH_3^+ + NH_3$$
 (5)

The steady-state ion ratio is given by

$$(I_{18^+}/I_{76^+})_{\rm ss} = k_{-3}^{-1}/(k_5 N[t - C_4 H_9 N H_2])$$
(6)

Reaction 5 is an exothermic proton-transfer reaction, and k_5 can be calculated from the capture rate as 2.2×10^{-9} cm³/s at 600 K. The value of k_{-3}^{1} is then obtained from the observed steady-state ion ratios and eq 6, which yields the first-order rate constant for the decomposition. For a decomposition reaction at the low-pressure limite, the second-order activation rate constant

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reaction	k ^a	<i>P</i> (CH ₄) ^{<i>b</i>}	E_{a}^{c}	ΔH° ^c	Δ.S° ^c	T
2. $t - C_4 H_9^+ + NH_3 \rightarrow NH_4^+ + i - C_4 H_8$	1.2 ± 0.4	1.4-3.7		-12.9 ± 1	-5.8 ± 2	600
$-3. t - C_4 H_9 N H_3^+ \rightarrow N H_4^+ + i - C_4 H_8$			29.1	34.9	39.2	
	0.00038	1.6-4.4				676
	0.00021	2.6				660
	0.00012	2.2				638
	0.000071	2.3				629
	0.000030	2.2				600
	0.000010	2.0-4.1				568
3. $NH_4^+ + i - C_4H_8 \rightarrow t - C_4H_9NH_3^+$			-6.0 ^e	-34.9	-39.2	
	2.01					676
	2.0 ^f					660
	2.4					638
	2.4					629
	3.8					600
	6.4					570
	4.48					551
4. $t - C_4 H_9^+ + N H_3 \rightarrow t - C_4 H_9 N H_3^+$				-46.5	-44.0	

TABLE I: Kinetic and Thermochemical Parameters

^a For reaction 2, second-order rate constant in units of 10^{-9} cm³/s; reaction -3, the listed k in units of 10^{-9} cm³/s is the second-order rate constant $k_{-3}^2 = k_{-3}^{-1}/N(CH_4)$ as calculated from the measured rate constant k_{-3}^{-1} . For reaction 3, third-order rate constants in units cm⁶/s. ^bUnits of Torr. Pressure ranges indicate pressures between which k was independent of pressure. ${}^{c}E_{a}$ and ΔH^{o} in units of kcal/mol; ΔS^{o} in units of cal/(mol K). ^d Units of kelvin. Calculated from $\Delta H^{o}_{3} = E_{a,3} - E_{a,-3}$. Third-order association rate constant in units of 10^{-29} cm³/s, calculated from the decomposition rate constant k_{-3} ; and the equilibrium constant K_3 calculated from $\exp((\Delta H^o_3 - T\Delta S^o_3)/T)$. *Obtained directly from the association reaction in Figure 3.



Figure 4. Arrhenius plot for k_{-3} for the decomposition reaction *t*-C₄H₉NH₃⁺ \rightarrow NH₄⁺ + *i*-C₄H₈ measured in a mixture containing 0.0044% t-C4H9NH2 plus 0.034% C6H6 in CH4 at total pressures of 2.0-2.5 Torr. Rate constants k_{-3} calculated from steady-state concentrations according to eq 6.

is then calculated as $k_{-3}^2 = k_{-3}^1/N[CH_4]$. Recently, we investigated⁸ the thermal decomposition of $C_2H_5OH_2^+$ and several protonated ethers^{9,10} and found some of the reactions to be at the low-pressure limit and others at the high-pressure limit under our conditions. Similarly, the decomposition of $t-C_4H_9NH_3^+$ may be at the low-pressure limit, the high-pressure limit, or in the falloff region. We verified the behavior in this system by measuring k_{-3}^2 at several pressures at 676 K. Typical results (Figure 3) exhibit a linear dependence on P with a slope of zero, indicating that the reaction is at the low-pressure limit. Similarly, k_{-3}^2 was found to be independent of CH₄ pressure between 2 and 4 Torr at 575 K. The temperature dependence of k_{-3}^2 shown in the Arrhenius plot in Figure 4 gives the low-pressure limiting activation energy as $E_{a,-3} = 29.1$ kcal/mol, which is considerably lower than the endothermicity of the reaction. Such a finding is common for low-pressure activation energies. This result can be used in conjunction with RRKM calculations to obtain the potential energy barrier for reaction -3, which relates to the energy barrier to the reverse condensation reaction, as discussed in the next section.

Condensation of NH_4^+ with i- C_4H_8 . The addition of NH_4^+ to $i-C_4H_8$, i.e., reaction 3, is best observed in a mixture containing



Figure 5. Time-resolved normalized ion intensities in a mixture of 0.012% NH₃ and 0.22% *i*-C₄H₈ in CH₄ at 551 K, total pressure 2.32 Torr. The plots show the association of NH_4^+ with *i*-C₄H₈.

NH₃ and *i*-C₄H₈ at a sufficiently low temperature that the reverse decomposition, reaction -3, is negligible. The ion profiles under appropriate conditions are shown in Figure 5. Although $t-C_4H_9^+$, derived from exothermic chemical ionization processes, is evident at short times, the adduct $t-C_4H_9NH_3^+$ is not formed from $t-C_4H_9^+$ reacting with NH₃ since the association channel in that system is negligible, and the formation of $t-C_4H_9NH_3^+$ continues after $t-C_4\overline{H}_9^+$ decays (Figure 5).

Our assumption that the ion formed at m/z 74 (empirical formula $C_4H_{12}N^+$) has the t- $C_4H_9NH_3^+$ structure rather than other isomeric forms is based on thermochemical considerations. The only other likely candidate is protonated isobutylamine, which is less stable by 7 kcal/mol than $t-C_4H_9NH_3^+$ in terms of ΔH°_{f} . Although S° (*i*-C₄H₉NH₃⁺) is more positive than $S^{\circ}(t C_4H_9NH_3^+$) by approximately 5.5 cal/(mol K), giving a $T\Delta S$ value of ~3.6 kcal/mol at 600 K favoring $i-C_4H_9NH_3^+$, the combined difference in $\Delta G^{\circ}(\Delta H^{\circ} - T\Delta S^{\circ})$ still favors t- $C_4H_9NH_3^+$ by more than 3 kcal/mol in this temperature range.

The value of k_3 can be obtained directly from ion profiles such as those shown in Figure 5. At higher temperatures where the system comes to equilibrium, k_3 can also be calculated from the approach to equilibrium in the complex system illustrated in Figure 4. More simply, k_3 can be derived from the relation $K_3 = k_3/k_{-3}$, using k_{-3} as measured from the decomposition of $t-C_4H_9NH_3^+$. Since reaction -3 is at the low-pressure limit, i.e., second order, reaction 3 must be third order, and $k_3^3 = k_3^2/N(CH_4)$. Table I gives values of k_3^3 obtained in this manner at the same tem-

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Figure 6. Time-resolved normalized ion intensities in a mixtures of 0.011% NH₃ and 1.07% *i*-C₄H₈ in CH₄ at 629 K, total pressure 2.58 Torr. The plots show an equilibrium system with proton transfer connecting NH₄⁺ and *t*-C₄H₉⁺ and association/decomposition connecting NH₄⁺ and *t*-C₄H₉NH₃⁺.

peratures where k_{-3} was measured.

Reaction 3 is the activated insertion of an ion into a double bond. The activation energy may be obtained from eq 7.

$$\Delta H^{\circ}_{3} = -R \, \mathrm{d}(\ln k_{3})/\mathrm{d}(1/T) = -R \, \mathrm{d}(\ln (k_{3}/k_{-3}) = E_{a,3} - E_{a,-3}$$
(7)

As is common for the three-body association reaction, $E_{a,3}$ is negative. From a plot of log k_3 vs log T, the temperature coefficient may be expressed alternatively as $k = AT^{-10.8}$. Such large negative temperature coefficients are also common to three-body ion-molecule association reactions.

Equilibria in $NH_3 + i-C_4H_8$ Mixtures. Typical ion profiles found in mixtures of $i-C_4H_8$ and NH_3 in methane at 629 K are illustrated in Figure 6. Fast chemical ionization processes generate mainly $t-C_4H_9^+$, which undergoes reaction 2 to generate NH_4^+ . The adduct ion $t-C_4H_9NH_3^+$ also forms with increasing time, and the three major ions NH_4^+ , $t-C_4H_9^+$, and $t-C_4H_9NH_3^+$ eventually reach time-independent equilibrium concentrations.

The reactions connecting the ions in the equilibrium system can be identified by using the preceding observations. NH_4^+ is produced by the decomposition of $t-C_4H_9NH_3^+$, reaction -3, and by the proton-transfer reaction 2. The ion $t-C_4H_9^+$ is produced by the reverse proton transfer (-2) which is its only major source since it is not a significant decomposition product of $t-C_4H_9NH_3^+$. The ion $t-C_4H_9NH_3^+$ is formed by the condensation reaction 3 and, as noted above, not by the addition of $t-C_4H_9^+$ to NH_3 . In summary, NH_4^+ is in equilibrium with $t-C_4H_9^+$ through

In summary, NH_4^{+} is in equilibrium with $t-C_4H_9^{-}$ through reactions 2 and -2 and with $t-C_4H_9NH_3^{+}$ through reactions 3 and -3. The latter two ions are therefore also in equilibrium, via indirect paths.

Thermochemistry of Proton Transfer between $t-C_4H_9^+$ and NH_3 . The equilibrium constant K_2 is obtained in the usual manner from the relative ion intensities of NH_4^+ and $t-C_4H_9^+$. The usual checks were performed to assure that K_2 was independent of mixture composition and ion source pressure. Typically, NH_3 constituted 0.00005–0.0001 and $i-C_4H_8$ 0.002–0.05 mole fraction of the mixture in methane, and the ratios of the two reactants were 1:200 to 1:1000. Total source pressures varied between 2.0 and 4.5 Torr. The involvement of the association reaction limited the concentrations of the reactants to the low values stated. However, at these concentrations, reactions times up to the longest observable time of 2–4 ms were required to reach equilibrium at low temperatures where K is large, which limited the temperature range of the measurements to 550–680 K.

A van't Hoff plot for equilibrium (2) is shown in Figure 7. Due to the restricted temperature range, the temperature study was repeated five times. The values found for ΔH° were 13.6 ± 0.5 , 13.0 ± 0.2 , 13.0 ± 0.2 , 12.2 ± 0.3 , and 12.1 ± 0.1 kcal/mol, the error representing the standard deviation of the slope of the van't



Figure 7. van't Hoff plots for (A) $t-C_4H_9^+ + NH_3 \leftrightarrow NH_4^+ + i-C_4H_8$; (B) $NH_4^+ + i-C_4H_8 \leftrightarrow t-C_4H_9NH_3^+$; (C) $t-C_4H_9^+ + NH_3 \leftrightarrow t-C_4H_9NH_3^+$, measured in a mixture of 0.012% NH_3 and 0.22% $i-C_4H_8$ in CH_4 , at a total pressure of 2.6 Torr.

Hoff plot in each measurement. The average value is 12.8 ± 0.8 kcal/mol, the error representing the reproducibility of the result. In addition to random errors, systematic error may result from inaccurate temperature measurements. We recently recalibrated our thermocouples and found no discrepancies and also remeasured ΔH° for several association equilibria. The results were consistent with published values from other laboratories as described elsewhere.⁴ These checks verified that the systematic error is less than 5%, i.e., 0.8 kcal/mol.

In addition to the direct measurement of equilibrium (2), we also bridged the PA difference through $(C_2H_5)_2CO$, $CH_3COO-C_2H_5$, CH_3SCH_3 , and $CF_3CH_2NH_2$ by variable-temperature equilibria and found 12.6, 13.2, 12.3, and 11.2 kcal/mol. These agree well with the direct measurement and yield an average value of 12.3 kcal/mol. Therefore, with a liberal error estimate, our result is 12.5 ± 1 kcal/mol.

The value of ΔS° is obtained from $\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ})/T$. The determination of $\Delta G^{\circ} = -RT \ln K$ values may include systematic errors due to uncertainties in reactant concentration and mass discrimination. Replicate measurements yielded -6.9, -6.5, -5.8, and -5.8 cal/(mol K). With a liberal error estimate, the net result is -6.2 \pm 2 cal/(mol K). The bridging experiments listed above gave an average value of 5.9 cal/(mol K). Again, this agrees well with the direct measurement and gives an overall average value of -6.1 \pm 2 cal/(mol K). Statistical mechanical tables give $\Delta S^{\circ}(NH_3 \rightarrow NH_4^+) = -1.5$ cal/(mol K) at 600 K.¹¹ From equilibria against several reference compounds, we found ΔS° for the other half-reaction $t \cdot C_4H_9^+ \rightarrow i \cdot C_4H_8$ as -2.4 ± 1.5 cal/(mol K). Therefore, the combined expected value is $\Delta S^{\circ}_2 = -3.9$ cal/(mol K), in good agreement with the experimental value.

The proton affinity of *i*-C₄H₈ has been established from theshold measurements as 195.9 kcal/mol at 300 K.¹ Combined with the present results, this yields $PA(NH_3) = 208.4 \text{ kcal/mol}$, which is substantially higher than the value of 204.0 kcal/mol adopted in a recent evaluated tabulation.¹ On the other hand, it is in good agreement with, and in fact still somewhat lower than, a high-level ab initio value of 210.0 kcal/mol.¹²

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There are no other published variable-temperature equilibria data available that tie ammonia directly or indirectly to a primary reference standard such as isobutene. However, Kebarle and co-workers¹³ constructed an interlocking ladder of ΔG° values connecting ammonia and isobutene at 600 K, which is in the temperature range of the present measurements, and used the same technique. They would predict a ΔG° for reaction 2 of -8.1 kcal/mol based on their multiple-bridging results. Our ΔH° and ΔS° values of -12.5 kcal/mol and -6.1 cal/(mol K) convert to a ΔG°_{600} of -8.8 kcal/mol, which corresponds to an equilibrium constant which is higher by a factor of 2 than that which would be predicted by the data from Kebarle's laboratory at 600 K. Considering the differing instrumentation, which may shift individually measured equilibrium constants up or down by a constant factor due to relative ion transmission coefficients, detector response, etc. (this does not affect the slopes of van't Hoff plots), the agreement between the two sets is quite acceptable.

The adduct ion $t-C_4H_9NH_3^+$ is in equilibrium with NH_4^+ through reaction 3 and also with $t-C_4H_9^+$, where equilibria (2) and (3) cause (4) to also be equilibrium under appropriate conditions. van't Hoff plots are shown in Figure 7. Duplicate measurements gave $\Delta H^{\circ}_{3} = -34.8 \pm 0.6$ and -35.1 ± 0.8 kcal/mol, i.e., an average of 34.9 ± 1 kcal/mol compared with -31 kcal/mol from tabulated values.¹ For ΔH°_{4} we performed four replicate measurements. The results were $-47.8 \pm 1.0, -46.2$ \pm 2.2, -47.0 \pm 1.0, and -45.6 \pm 0.3 kcal/mol, giving an average of -46.5 kcal/mol, which is to be compared with -39 kcal/mol from tabulated values. The present results are derived from steep van't Hoff plots obtained over a narrow range of high temperatures where precise temperature measurement is difficult. Therefore, the error limit is probably on the order of ± 2 kcal/mol. The results give $\Delta H^{\circ}_{f}(t-C_{4}H_{9}NH_{3}^{+}) = 108.3 \text{ kcal/mol} (\text{using } \Delta H^{\circ}_{f}(NH_{4}^{+})$ = 146.3 kcal/mol from our proton-transfer equilibria), compared with the tabulated value of 116 kcal/mol, and $PA(t-C_4H_9NH_2)$ = 228.7 kcal/mol, compared with the tabulated value of 220.8 kcal/mol. Again, the present results are significantly higher than the tabulated proton affinities. McMahon et al.¹⁵ have recently reproduced both the ΔH° and ΔS° values for the association equilibrium within our error limits.

The expected ΔS° values at 600 K may be estimated as follows. We use $S^{\circ}(NH_3) = 52.7$, $S^{\circ}_{600}(NH_4^+) = S^{\circ}(NH_3) - 1.5 = 51.2$, $S^{\circ}(i-C_4H_8) = 89.7$, $S^{\circ}(t-C_4H_9^+) = S^{\circ}(i-C_4H_8) + 2.4 = 92.1$, and $S^{\circ}(t-C_4H_9NH_3^+) = S^{\circ}(t-C_4H_9NH_2) - R \ln 3 = 107.7 - 2.2 =$ 105.5 cal/(mol K), where S° for the neutrals is from Stull et al.,¹⁴ and R ln 3 results from the creation of an internal NH₃ rotor upon converting $t-C_4H_9NH_2$ to $t-C_4H_9NH_3^+$. These values yield an expected value of $\Delta S^{\circ}_3 = -35.4$ cal/(mol K) compared with the measured value of -39.2 cal/(mol K), and an expected $\Delta S^{\circ}_4 =$ -39.6 cal/(mol K) compared with the measured value of -43.8 cal/(mol K) (from an average of three measurements giving -45.6, -43.6, and -43.3 cal/(mol K)). Again, because of the steep van't Hoff plots taken over a narrow range, the probable uncertainty in the measured ΔS° is ± 4 cal/(mol K). Within these limits the measured values agree with the estimated expected values.

In order to verify the PA for $t-C_4H_9NH_2$ derived from the condensation equilibria (3) and (4), we also connected $i-C_4H_8$ with $t-C_4H_9NH_2$ through an interlocking ladder of proton-transfer equilibria involving 27 compounds. Although the results will be reported in detail elsewhere,⁴ a typical path between $i-C_4H_8$ and $t-C_4H_9NH_2$, with experimental $-\Delta H^\circ$ values given in [] and PA values from the optimized ladder for the intermediate compounds given in (), and referenced to $PA(i-C_4H_8) = 195.9 \text{ kcal/mol}$, is as follows: $i-C_4H_8$ (195.9) \rightarrow [2.2] CH₃COCH₃ (198.4) \rightarrow [0.7] CH₃COOCH₃ (199.2) → [4.5] (C₂H₅)₂CO (203.6) → [5.2] NH₃ $(208.4) \rightarrow [5.0]$ pyrrole $(213.4) \rightarrow [2.1]$ 2-F-pyridine $(215.7) \rightarrow$ [3.9] CH_3NH_2 (219.6) \rightarrow [1.1] 3-F-pyridine (220.7) \rightarrow [2.4] $C_2H_5NH_2$ (223.4) \rightarrow [2.9] *i*- $C_3H_7NH_2$ (226.5) [1.4] pyridine $(227.6) \rightarrow [1.3] t-C_4H_9NH_2$ (229.2 kcal/mol). These PA values are significantly higher than those currently recommended,¹ but the resulting PA for $t-C_4H_9NH_2$ is in excellent agreement with the value derived from the condensation equilibrium (4). Our PA values for the molecules between $i-C_4H_8$ and NH₃ have also been reproduced recently by McMahon et al.¹⁵

Summary

This work is the first kinetic study of the thermally activated covalent condensation of an ion with an olefinic bond. The reverse decomposition is also observed, adding to a still small list of reported ion pyrolysis reactions. The decomposition is at the low-pressure limit, and measured activation energies in such systems can be combined with RRKM calculations in the future to calculate the threshold for decomposition. Such studies can clarify whether the addition of an ion into an olefinic bond has an activation barrier.

Temperature-dependent equilibrium studies on the $t-C_4H_9^+/NH_4^+$ system offer a new way to measure the thermochemistry of the ammonium ion, avoiding sources of error present in some other methods. Similarly, association equilibria leading to adducts such as as $t-C_4H_9NH_3^+$ allow the evaluation of ion thermochemistry in the upper part of the proton affinity scale, where absolute standards from threshold measurements are lacking. In this respect, Lias et al. state that, "None of the standards (for the upper proton affinity scale) can be considered to have a firmly-enough established proton affinity that it could be stated with certainty that future variations in absolute assignments will not occur."¹ The present results show that significant changes from the tabulated PA values in the upper range are indeed necessary.

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Registry No. *i*-C₄H₈, 115-11-7; NH₃, 7664-41-7; *t*-C₄H₉NH₂, 75-64-9; NH₄, 14798-03-9; *t*-C₄H₉NH₃, 22534-19-6; C₄H₉, 14804-25-2.

⁽¹³⁾ The complete interlocking ΔG° ladder is given in: Kebarle, P. Annu. Rev. Phys. Chem. 1977, 28, 445. The original data is from: Lau, Y. K.; Kebarle, P. J. Am. Chem. Soc. 1976, 98, 7452. Yamdagni, R.; Kebarle, P. J. Am. Chem. Soc. 1976, 98, 1320.

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