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Generation of Covalent and Electrostatic Complexes in Association Reactions of *tert*-Butyl Cation with Small Organics

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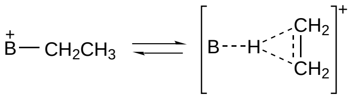
Abstract: Pulsed ionization High-Pressure Mass Spectrometry (PHPMS) has been used to investigate the thermochemistry of the association reactions of t-$C_4H_9^+$ with various neutral molecules in the gas phase. The behavior of the logarithm of the association equilibrium constant as a function of inverse reaction temperature (a van't Hoff plot) has been examined over a broad temperature range to yield accurate thermochemical data for the enthalpy and entropy of association. All of the systems investigated show either a pronounced break or a subtle curvature in the van't Hoff plot. This behavior is consistent with two coexisting isomeric forms of the association adduct, *viz,* (i) a low-temperature, covalently bound isomer characterized by larger $-\Delta H°$ and $-\Delta S°$ values and (ii) a high-temperature, electrostatically bound isomer of lower $-\Delta H°$ and $-\Delta S°$ values. Experimental thermochemical data for the association reactions are reported. From the low-temperature data, proton affinities (PA) of t-$C_4H_9OCH_3$ (205.1 kcal/mol) and t-$C_4H_9OC_2H_5$ (214.0 kcal/mol) were determined. *Ab initio* calculations carried out in conjunction with the experimental study of some of these association reactions support the experimental results. The results obtained for t-$C_4H_9^+$ onto $(CH_3)_2O$ revealed the existence of two broad energy plateaus when attempting to optimize different electrostatically bound adduct structures. Structures corresponding to these energy plateaus are proposed to be possible transition states characterized by unconventional ionic hydrogen bonds. Theoretical thermochemical data for the association reactions investigated are reported.

Introduction

Many workers have investigated reactions which have been shown to occur through the intermediacy of ion−neutral complexes.[1−5] Some of these complexes, which are bound predominantly by electrostatic forces (ion−dipole or ion−induced dipole interactions), have the capability to isomerize into energetically more favored ions and to decompose *via* less energy demanding pathways. A central theme in many such isomerizations is the concept of ion−neutral reorientation, which can frequently be probed *via* isotopic labeling experiments.

Hydrogen-bonded complexes, such as proton-bound dimers, are well-known species which are well characterized from ion−molecule equilibrium studies. Others, such as π-complexes, are also electrostatically bound complexes. Morton[5] has proposed a classification which allows a distinction between an ion−neutral complex, a hydrogen-bonded complex, and a π-complex by using the cyclopentyl cation/phenoxy radical system as an example. "In a π-complex two geminal methylene hydrogens retain non-equivalence, but the two acidic *cis*-hydrogens on different carbons will be equivalent. In a hydrogen-bonded complex one acidic hydrogen is distinct from all the others, although it may become equivalent with a geminal hydrogen on the same methylene. The motion that renders all four acidic hydrogens equivalent satisfies the reorientation criterion. Such an equivalence would be characteristic of an ion−molecule complex." Thus the reorientation criterion is put forth as a characteristic for ion−neutral complexes but not characteristic for hydrogen-bonded complexes or π-complexes.

There are many examples of complexes bound by electrostatic forces involving proton bridged species. For example, the complex between H_2O and the symmetrical proton-bridged ethene[6] has been shown to exist. This symmetrical non-classical form lies *ca.* 12 kcal/mol higher in energy than the form corresponding to protonated ethanol ($B = H_2O$, eq 1).[7,8]

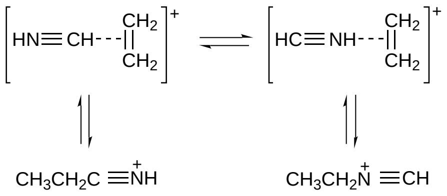


$$\overset{+}{B}-CH_2CH_3 \rightleftharpoons \left[B\cdots H\begin{matrix}\cdot\cdot CH_2\\ \| \\ \cdot\cdot CH_2\end{matrix}\right]^+$$

(1)

Zagorevskii *et al.*[9] have investigated this system for $B = CH_3CH_2X$ (X = Cl, Br, I) and concluded from the ion−molecular reactions investigated that both structures are produced in different proportions depending upon the halogen involved.

Bouchoux *et al.*[10] have shown that protonated ethyl cyanide and protonated ethyl isocyanide isomerize to an electrostatically bound complex between C_2H_4 and $HCNH^+$, as shown in eq 2, which may dissociate further or interconvert by reorientation.



$$\begin{tikzcd}\left[HN\equiv CH\cdots\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}\right]^+ \arrow[r, shift left, harpoon] \arrow[d, shift left, harpoon] & \left[HC\equiv NH\cdots\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}\right]^+ \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon] \\ CH_3CH_2C\equiv\overset{+}{N}H \arrow[u, shift left, harpoon] & CH_3CH_2\overset{+}{N}\equiv CH \arrow[u, shift left, harpoon]\end{tikzcd}$$

(2)

Liehr *et al.*[11] have investigated the chemistry of the association adduct between t-$C_4H_9^+$ and $C_6H_5CH_2OH$ and proposed

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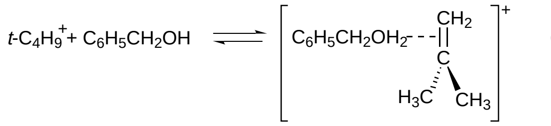
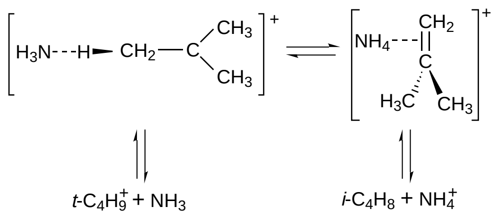
an electrostatically bound complex, as shown in eq 3, to be the precursor for further decomposition, *i.e.* loss of H_2O.



$$t\text{-}C_4H_9^+ + C_6H_5CH_2OH \rightleftharpoons [C_6H_5CH_2OH_2\cdots CH_2{=}C(CH_3)_2]^+ \quad (3)$$

Morton[1] has discussed the association reaction between t-$C_4H_9^+$ and NH_3 and proposed two kinds of electrostatically bound complexes for the association adduct, as shown in eq 4.



(4)

By use of PHPMS (Pulsed ionization High-Pressure Mass Spectrometry) it is possible to measure equilibrium constants for gas-phase ion−molecule reactions as a function of temperature, which effectively leads to a measurement of the enthalpy and entropy changes, eq 5, associated with either the exchange reaction, eq 6, or clustering reaction, eq 7, studied.

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

$$AC^+ + B \rightleftharpoons A + BC^+ \quad (6)$$

$$A^+ + B \rightleftharpoons AB^+ \quad (7)$$

Examination of the thermochemistry of the association of an ion with a neutral molecule is a powerful tool for the inference of gross structural features of an ion−molecule adduct. The magnitude of the enthalpy and entropy changes can often, with the aid of chemical intuition, be used to give valuable information about the structure of the adduct ion.

When investigating equilibrium reactions over an extended temperature range either a break or a curvature in the van't Hoff plot of ln K_{eq} *vs* $1/T$ can be observed if one of the participants in the equilibrium can exist in more than one isomeric form, dependent on the temperature. Several examples, mainly from this laboratory, clearly illustrate how powerful this technique is, and how common it has become to observe isomeric forms of ionic species in the gas phase using PHPMS. In the present study several examples of experiments are given to emphasize the generality and usefulness of the technique.

It has been previously demonstrated that the PHPMS technique can be used to implicate the existence of highly sterically congested structures of adducts derived from the addition of either dimethyl ether or acetone to methylated acetone.[12] A further investigation of these systems (over a more extended temperature range) revealed breaks in the van't Hoff plots, consistent with two distinct isomeric forms of the association adducts.[13] Based on the magnitude of the reaction enthalpies and entropies and the presence or absence of equilibrium deuterium isotope effects, the isomeric forms were identified and proposed to be (i) a low-temperature, covalently bound isomer characterized by larger $-\Delta H^\circ$ and $-\Delta S^\circ$ values and significant equilibrium isotope effects on the entropy of association, and (ii) a high-temperature, electrostatically bound isomer of lower $-\Delta H^\circ$ and $-\Delta S^\circ$ values and with insignificant equilibrium isotope effects.

In an independent study, a break in the van't Hoff plot was observed in the proton exchange reaction between pyrrole and 4-methoxy-1-butanol.[14] Once again, using the magnitude of the reaction enthalpy and entropy, two isomeric forms of $[CH_3O(CH_2)_4OH]H^+$ were identified and proposed to be (i) a high-temperature, methoxy-protonated isomer characterized by lower $-\Delta H^\circ$ and $-\Delta S^\circ$ values,[15] and (ii) a low-temperature, intramolecularly proton bound isomer of higher $-\Delta H^\circ$ and $-\Delta S^\circ$ values.[16] Not surprisingly, the association reaction between $[CH_3O(CH_2)_4OH]H^+$ and $CH_3O(CH_2)_4OH$ also showed a break in the van't Hoff plot, due to the same isomeric forms of $[CH_3O(CH_2)_4OH]H^+$, with a high-temperature isomeric form characterized by lower $-\Delta H^\circ$ and $-\Delta S^\circ$ values,[17] and a low-temperature isomeric form of higher $-\Delta H^\circ$ and $-\Delta S^\circ$ values.[18]

In yet another experiment, a break in the van't Hoff plot has been observed in the association reaction of protonated L-dimethyl tartrate onto L-dimethyl tartrate.[19] Using the same method, two isomeric forms of the protonated L-dimethyl tartrate were characterized and can be proposed to be (i) a high-temperature, carbonyl-protonated L-dimethyl tartrate characterized by lower $-\Delta H^\circ$ and $-\Delta S^\circ$ values,[20] and (ii) a low-temperature, intramolecular proton bound isomer of higher $-\Delta H^\circ$ and $-\Delta S^\circ$ values.[21]

Even though the PHPMS method has clearly proven to be a powerful tool for the inference of structural features of gaseous cluster ions, only four other cases of direct observation and thermochemical characterization of interconversion of ionic isomers have been reported. In the first of these, Hiraoka and Kebarle[22] observed, also by use of PHPMS, a low-temperature, weakly bound adduct between $C_2H_5^+$ and H_2 which overcame a small activation barrier at higher temperatures to yield a covalently bound $C_2H_7^+$ species. The isomeric forms were characterized by the magnitude of the $-\Delta H^\circ$ and $-\Delta S^\circ$ values. In the second case, Sunner *et al.*[23] observed a break in the van't Hoff plot, again using PHPMS, in the association reaction between t-$C_4H_9^+$ and i-C_4H_{10} which they ascribed to a transition between a tight, covalently bound, adduct at low temperature and a "loose", more weakly bound, adduct at higher temperature. Once again, both isomeric forms were thermochemically characterized. In the third case, Bushnell *et al.*[24] observed, in a high-pressure experiment, a covalent and an electrostatic form of the association adduct between Sc^+ and H_2. Both isomeric forms were thermochemically characterized. In the fourth case, Anicich *et al.*[25] reported a study of CH_3^+ clustering onto HCN in which two isomers were observed: one *via* radiative stabilization, $[CH_3NCH]^+$, and one by collisional stabilization, $[CH_3CNH]^+$.

Little work has been done theoretically on the studies of the temperature dependence of the enthalpy changes for a given

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[12] Szulejko, J. E.; Fisher, J. J.; McMahon, T. B.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 147.

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[14] Szulejko, J. E.; McMahon, T. B. Unpublished results from this laboratory.

[15] $\Delta H^\circ = -7.5 \pm 1$ kcal·mol^{-1} and $\Delta S^\circ = -11.6 \pm 2$ cal·mol^{-1}·K^{-1}.

[16] $\Delta H^\circ = -12.1 \pm 1$ kcal·mol^{-1} and $\Delta S^\circ = -21.7 \pm 2$ cal·mol^{-1}·K^{-1}.

[17] $\Delta H^\circ = -33.5 \pm 1$ kcal·mol^{-1} and $\Delta S^\circ = -51.1 \pm 2$ cal·mol^{-1}·K^{-1}.

[18] $\Delta H^\circ = -28.0 \pm 1$ kcal·mol^{-1} and $\Delta S^\circ = -40.2 \pm 2$ cal·mol^{-1}·K^{-1}.

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[20] $\Delta H^\circ = -20.3 \pm 1$ kcal·mol^{-1} and ΔS° is unknown (unknown partial pressure).

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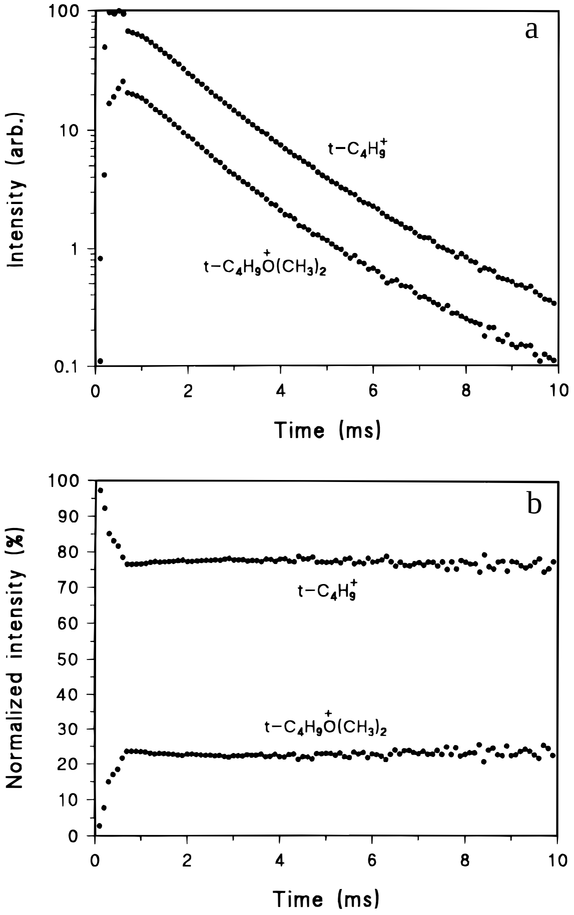

Figure 1. Variation of absolute ionic abundances of (a) and variation of normalized ionic abundances (b) of t-$C_4H_9^+$ and its $(CH_3)_2O$ association adduct as a function of time after a 500-μs electron beam pulse. A total of 1000 electron gun pulses were accumulated. Mixture composition: CH_4 (1005 Torr), i-C_4H_8 (1050 mTorr), and $(CH_3)_2O$ (640 mTorr) at 413 K (140 °C).

reaction. One such example is a simulated van't Hoff plot with a break in a recent publication by Asada *et al.*[26] Using a Monte Carlo calculation, they have shown that the association reaction, $Cl(H_2O)_2^- + H_2O \rightarrow Cl(H_2O)_3^-$, has a break at *ca.* 150 K, which was ascribed to a possible phase transition of the adduct ion.

In the current study, we have focused our attention on the association reactions of t-$C_4H_9^+$ with several small organics where isomerization may occur in order to investigate the thermochemistry, and thereby propose plausible structures for the adduct ions. The experimental and *ab initio* investigations of these association reactions are reported herein.

Experimental Section

Equilibrium Measurements. The measurements were made with a pulsed ionization high-pressure mass spectrometer, PHPMS, constructed at the University of Waterloo, which has been described in detail previously.[12]

Gas mixtures were prepared in a temperature-controlled 5-L reservoir using CH_4 as the bath gas to a pressure of 800−1000 Torr. Other components of the mixture were present at pressures less than 10 Torr in general. The gas mixture was bled into the ion source through a heated inlet line to a pressure of 5−9 Torr. Ionization was accomplished by a 10−500-μs pulse of 2-keV electrons focused into the ion source through a 150-μm aperture. Mass-selected ion temporal profiles were monitored by a PC-based multichannel scaler signal acquisition system configured at 20−100-μs dwell time per channel, depending on the persistence of the ion temporal profiles. A total of 250 channels were acquired using a duty cycle 10 ms longer than the residence time for the most persistent ion, which prevents pulse-to-pulse carry over in ion abundance. The results of 500−5000 electron gun pulses were accumulated, dependent on the signal intensity. Representative data are shown in Figure 1 for the association reaction of t-$C_4H_9^+$ onto $(CH_3)_2O$.

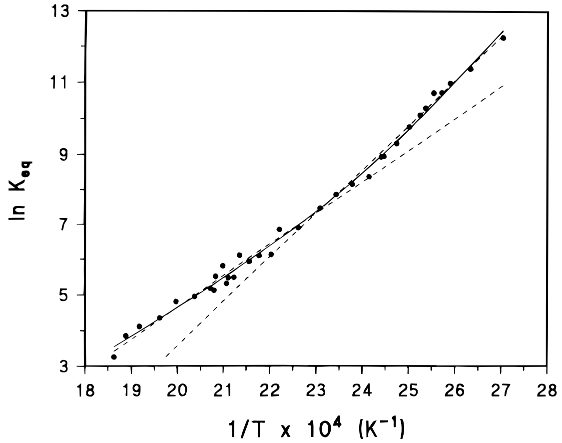

Figure 2. Van't Hoff plot for the association reaction of t-$C_4H_9^+$ onto CH_3OH. The solid line represents an exponential fit over the entire temperature range using four variables (ΔH_1°, ΔH_2°, ΔS_1°, and ΔS_2°; $N = 2$ in eq 8), and the dashed lines represent a fit using linear regression independently for the two temperature regimes (eq 5).

The t-$C_4H_9^+$ was generated by proton transfer chemical ionization to i-C_4H_8 or by dissociative chemical ionization of t-C_4H_9Cl. All materials used were commercial products of the highest purity obtainable.

***Ab Initio* Calculations.** All electronic structure calculations were carried out using the Gaussian 92[27] series of programs. Equilibrium geometries were optimized with the 6-31G(d) basis set[28−30] at the Hartree-Fock level (HF/6-31G(d)). Vibrational frequencies based on the harmonic oscillator approximation were computed at the HF/6-31G(d) level using the HF optimized geometries. No negative frequencies were found in any of the reported geometries. Total energies were calculated at the second-order Møller−Plesset perturbation theory level[31] (MP2/6-31G(d,p), frozen-core) for all systems and at the MP2/6-31G(2d,p) level of theory for the smaller systems (t-$C_4H_9^+$ onto CH_3OH and CH_3CN).

Results and Discussion

Thermochemical data for the association reactions of t-$C_4H_9^+$ onto CH_3OH, CH_3CN, C_2H_5OH, $(CH_3)_2O$, $(CH_3)_2CO$, and $(C_2H_5)_2O$ have been extracted from the van't Hoff plots (Figure 2−7) and tabulated (Table 1). All of the systems studied show either a pronounced break or a subtle curvature in the van't Hoff plot, consistent with the presence of two coexisting isomeric forms of the association adduct. Attempts to treat the

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(35) Szulejko, J. E. Unpublished results from this laboratory. Kinetic Method with C_2H_5OH and CH_3CN using HPMS.

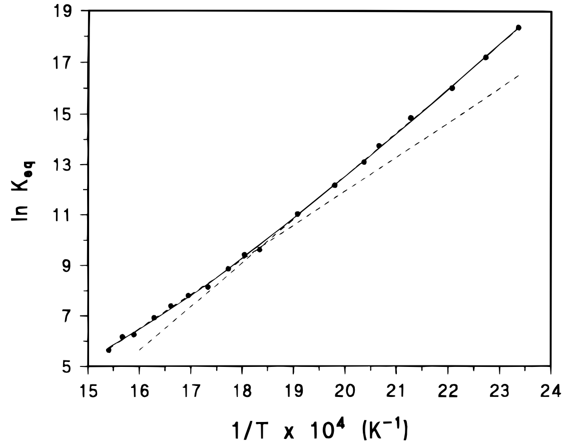


Figure 3. Van't Hoff plot for the association reaction of t-$C_4H_9^+$ onto CH_3CN. The solid line represents an exponential fit over the entire temperature range using four variables (ΔH_1°, ΔH_2°, ΔS_1°, and ΔS_2°; $N = 2$ in eq 8), and the dashed lines represent a fit using linear regression independently for the two temperature regimes (eq 5).

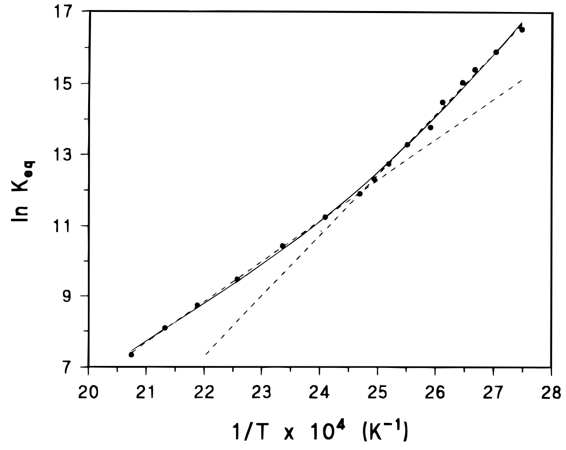


Figure 4. Van't Hoff plot for the association reaction of t-$C_4H_9^+$ onto C_2H_5OH. The solid line represents an exponential fit over the entire temperature range using four variables (ΔH_1°, ΔH_2°, ΔS_1°, and ΔS_2°; $N = 2$ in eq 8), and the dashed lines represent a fit using linear regression independently for the two temperature regimes (eq 5).

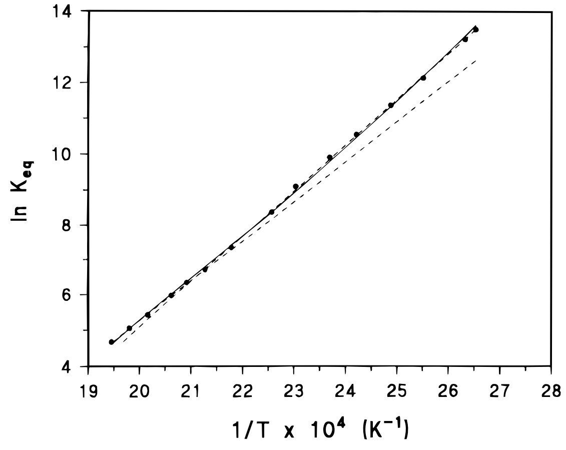


Figure 5. Van't Hoff plot for the association reaction of t-$C_4H_9^+$ onto $(CH_3)_2O$. The solid line represents an exponential fit over the entire temperature range using four variables (ΔH_1°, ΔH_2°, ΔS_1°, and ΔS_2°; $N = 2$ in eq 8), and the dashed lines represent a fit using linear regression independently for the two temperature regimes (eq 5).

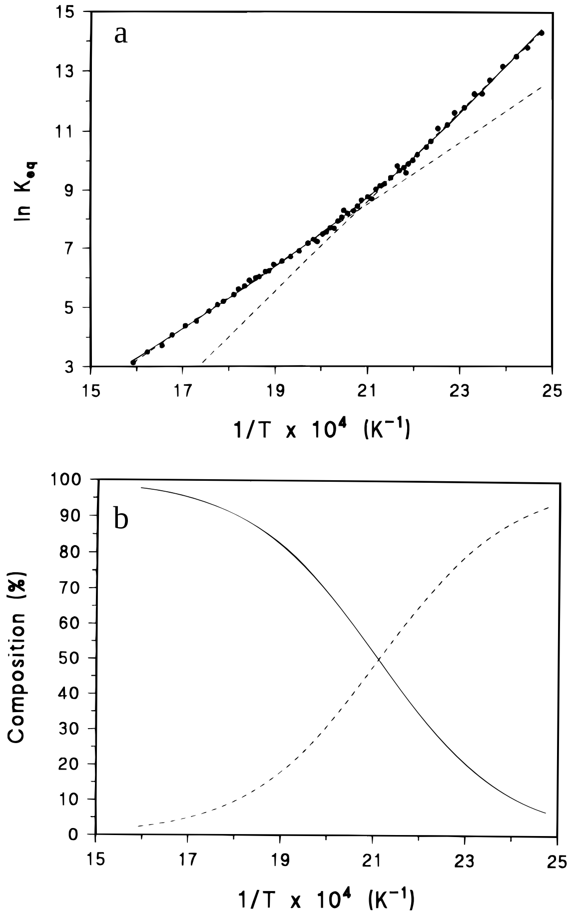


Figure 6. (a) Van't Hoff plot for the association reaction of t-$C_4H_9^+$ onto $(CH_3)_2CO$. The solid line represents an exponential fit over the entire temperature range using four variables (ΔH_1°, ΔH_2°, ΔS_1°, and ΔS_2°; $N = 2$ in eq 8), and the dashed lines represent a fit using linear regression independently for the two temperature regimes (eq 5). (b) Calculated (eq 9) composition for the two coexisting isomeric forms of the association adduct from the association reaction of t-$C_4H_9^+$ onto $(CH_3)_2CO$. Dashed line: low-temperature isomer. Solid line: high-temperature isomer.

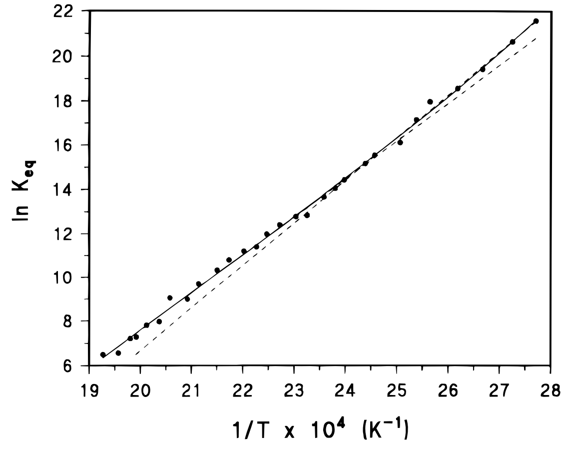


Figure 7. Van't Hoff plot for the association reaction of t-$C_4H_9^+$ onto $(C_2H_5)_2O$. The solid line represents an exponential fit over the entire temperature range using four variables (ΔH_1°, ΔH_2°, ΔS_1°, and ΔS_2°; $N = 2$ in eq 8), and the dashed lines represent a fit using linear regression independently for the two temperature regimes (eq 5).

two temperature regimes separately using linear regression to fit the data points as had been done previously, according to eq 5, turned out to be very misleading. Using independent linear regressions, it was assumed that the contribution from the other isomer was negligible. Based on this assumption, the thermochemical data made little sense. If, instead, the opposite was assumed, *i.e.* that in one temperature regime there is a considerable contribution from the other isomer, eq 8 can be

Table 1. Experimentally Obtained Thermochemical Data (298 K) for the Association Reaction of *t*-$C_4H_9^+$ onto Several Bases (B)

			high temperature		low temperature		
B	μ(B),[a] D	PA(B), kcal/mol	$-\Delta H°$,[e] kcal/mol	$-\Delta S°$,[e] cal/(mol·K)	$-\Delta H°$,[e] kcal/mol	$-\Delta S°$,[e] cal/(mol·K)	$-\Delta S°$(estimate),[f] cal/(mol·K)
CH_3OH	1.70	181.7[b]	15.1	21.1	29.1	54.0	50.1
CH_3CN	3.92	187.0[c]	20.4	20.5	35.0	45.4	46.0
C_2H_5OH	1.69	187.0[d]	20.4	27.6	38.6	72.9	50.4
$(CH_3)_2O$	1.30	189.6[b]	23.2	36.0	33.2	62.1	49.6
$(CH_3)_2CO$	2.88	194.2[c]	19.2	24.2	33.5	54.4	45.2
$(C_2H_5)_2O$	1.15	199.2[b]	33.7	52.4	46.3	86.4	50.2

[a] Dipole moments from ref 32. [b] Reference 33 (reevaluated value for $(C_2H_5)_2O$). [c] Reference 34. [d] Reference 35. [e] The estimated experimental uncertainty for $\Delta H°$ is ± 0.5 kcal/mol and that for $\Delta S°$ is ±5 cal/(mol·K). [f] Estimated values from isoelectronic analogs using Benson's additivity scheme[36] based on data from ref 37.

Table 2. Calculated (Eq 9) Composition[a] for the Two Coexisting Isomeric Forms of the Association Adduct at Various Ion Source Temperatures

ion source temp, K	CH_3OH	CH_3CN	C_2H_5OH	$(CH_3)_2O$	$(CH_3)_2CO$	$(C_2H_5)_2O$
273	100:0	100:0	100:0	99:1	100:0	100:0
323	99:1	100:0	100:0	92:8	100:0	92:8
373	91:9	100:0	85:15	59:41	98:2	47:53
423	52:48	99:1	24:76	22:78	86:14	11:89
473	16:84	95:5	3:97	8:92	50:50	2:98
523	4:96	82:18	1:99	3:97	19:81	1:99
573	1:99	57:43	0:100	1:99	7:93	0:100
623	1:99	32:68	0:100	1:99	3:97	0:100
673	0:100	17:83	0:100	0:100	1:99	0:100

[a] % low temperature:% high temperature.

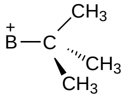
used to fit the data points:

$$\ln K^{\text{obs}}_{\text{eq},i} = \ln\left(\sum_{i=1}^{N}\exp\left(\frac{\Delta S_i^\circ}{R} - \frac{\Delta H_i^\circ}{RT}\right)\right) \qquad (8)$$

$$\frac{K_{\text{eq},i}}{\sum_{i=1}^{N} K_{\text{eq},i}} = \frac{\exp\left(\frac{\Delta G_i^\circ}{RT}\right)}{\sum_{i=1}^{N}\exp\left(\frac{\Delta G_i^\circ}{RT}\right)} \qquad (9)$$

were N is the number of isomers present. In the present work, $N = 2$ is assumed. Doing so, internally consistent thermochemical data are obtained, and furthermore, these data are in reasonable agreement with the *ab initio* calculations to be discussed later. From eq 9 we can calculate the isomeric composition as a function of temperature (Table 2) which takes the form of that illustrated in Figure 6b for the acetone adducts. The thermochemical data presented in Table 1 have been extracted from the van't Hoff plots (Figure 2−7) using eq 8 to fit the data points.

To distinguish between covalently and electrostatically bound association adducts, that is to determine whether the two isomers are two electrostatically bound association adducts, or if they are an electrostatically bound and a covalently bound association adduct, we have estimated the entropy changes for the formation of the covalently bound association adducts (Table 1) from Benson's[36] additivity schemes, based on data from ref 37. Since, presumably, the covalently bound isomer should represent the global minimum on the potential energy surface, the estimated values should be compared with the experimental values obtained from the low-temperature regime. The estimated values of $\Delta S°$ result in approximate entropy changes for the association reactions but without consideration of the steric congestion which leads to restriction of internal rotations about some of the single bonds of the covalent molecular framework. This means that the experimentally determined $-\Delta S°$ values for the adducts should, dependent upon the magnitude of the steric congestion of the base, be greater than or equal to the estimated values for the covalently bound association adducts which are formed. These covalently bound association adducts will hereafter be referred to as **I**.



I

Attempting to assign structures of the electrostatically bound association adducts is somewhat more complicated, since *t*-$C_4H_9^+$ can interact with a base in a variety of ways. It is fairly easy to distinguish between an orbiting complex, that is any adduct without a static structure, and a non-orbiting complex, that is any adduct with a relatively static structure. The $-\Delta H°$ and $-\Delta S°$ values for an association reaction forming an orbiting complex would be expected to be much less than those for an association reaction forming a non-orbiting complex. It has not been possible to find any examples of observations of orbiting complexes in the literature, and thus no representative thermochemical data were accessible. In order to estimate the order of magnitude of $-\Delta H°$ and $-\Delta S°$ for an association reaction forming an orbiting complex, we can consider the following example. One of the smallest observed documented changes in enthalpy and entropy of association for formation of a non-orbiting complex is from previous work[38] done in this laboratory. Using PHPMS it was found that the association reaction of Cl^- onto *c*-C_5H_{10} has a $-\Delta H°$ of 8.5 ± 0.2 kcal/mol and a $-\Delta S°$ of 19.9 ± 1 cal/(mol·K). Meot-Ner and Deakyne[39] found, also using PHPMS, that the association reaction of $(CH_3)_3NCH_3^+$ onto CH_3Cl has a $-\Delta H°$ of 6.5 ± 1 kcal/mol and a $-\Delta S°$ of 17.9 ± 2 cal/(mol·K). Based on this, the order of magnitude of $-\Delta H°$ and $-\Delta S°$ for an association reaction forming an orbiting complex is estimated to be less than or equal to these values. As is evident from Table 1, none of the values measured are of that magnitude; thus no orbiting complexes can be said to have been observed in the temperature regimes investigated here.

Depending upon base properties of the species involved, several types of isomeric electrostatically bound association adducts can be thought of as being possible, **II**−**VIII**:

In **II** the base interacts with a presumed non-classical form of *t*-$C_4H_9^+$. Non-classical carbocations, that is species with

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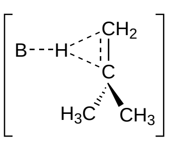
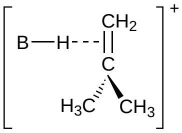
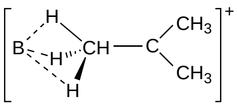


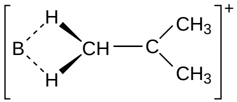
II



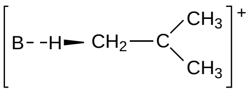
III



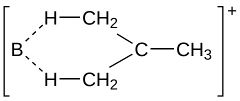
IV



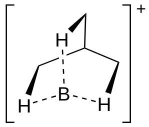
V



VI



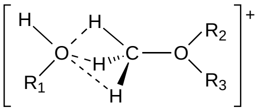
VII



VIII

bridging bonds described as three-center two-electron bonds, have been proposed frequently in the literature.[40−43] The first proposal of the formation of a pentavalent carbocation was that of Winstein and Trifan,[40,41] who proposed a non-classical structure for the norbornyl cation. Talrose *et al.*[42] were the first to observe the hypervalent carbocation, CH_5^+, and the hypervalent carbon cation $C_2H_7^+$ was observed by Wexler and Jesse.[43] The higher homologues become increasingly less stable with respect to dissociation to R^+ and H_2. The structure of the free t-$C_4H_9^+$ has, in a recent paper by Sieber *et al.*,[44] been calculated using high-level *ab initio* molecular orbital theory. They concluded that a C_s symmetric classical structure of the t-$C_4H_9^+$ represents the global minimum on the $C_4H_9^+$ potential energy surface and is stabilized by C−H hyperconjugation. This hyperconjugative stabilization is evident from the elongation of the C−H bonds, which are aligned parallel to the formally vacant 2p orbital on the central carbon and from the decrease of the corresponding (HCC) angles. The fact that the free t-$C_4H_9^+$ is a classical carbocation, does not rule out the possibility that it might also exist as a non-classical carbocation in an electrostatically bound association adduct like **II**. The hyperconjugatively stabilized t-$C_4H_9^+$ and the non-classical t-$C_4H_9^+$ are so similar in structure that, with an appropriate base, structures such as **II** could very easily exist (a few examples are given in the introduction for $C_2H_5^+$). An even more likely possibility is that **II** could be a transition state between some of the other proposed isomers.

In **III** the base is protonated and interacts with the π-system in i-C_4H_8 (mentioned in the introduction). The thermochemistry of this type of interaction has been investigated previously by Sunner *et al.*,[45] who have studied the thermochemistry of the association of K^+ onto C_6H_6 and found that the interaction was mainly electrostatic. Wojtyniak and Stone[46] found that the association reaction of $(CH_3)_3Si^+$ onto C_6H_6 results in a symmetric π-complex with C_{6v} symmetry in which rotational motion is not constrained. Meot-Ner and Deakyne[47] have also investigated several systems: NH_4^+, $CH_3NH_3^+$, $(CH_3)_3NH^+$, and $C_2H_5OH_2^+$ with aliphatic and aromatic π-donors. In a study pertinent to the present work Monteiro *et al.*[48] have investigated the dissociation of a variety of protonated ethers using MIKES (Mass analyzed Ion Kinetic Energy Spectrometry) and ICR (Ion Cyclotron Resonance spectrometry), and proposed, among other things, the existence of a complex **III**.



$R_1 = R_2 = R_3 = H$	(ref 49)
$R_1 = CH_3$, $R_2 = R_3 = H$	(ref 49)
$R_1 = R_2 = H$, $R_3 = CH_3$	(ref 49)
$R_1 = R_2 = CH_3$, $R_3 = H$	(ref 50)

IX

In **IV** the base interacts with a cavity of partially charged hydrogens created by one methyl group. This type of electrostatically bound adduct has, based on *ab initio* calculations, been previously proposed in the literature[49,50] for compounds with similar molecular framework, **IX**.

In **V** the interaction is between the base and two partially charged hydrogens from one of the methyl groups, whereas the interaction in **VI** is between the base and only one partially charged hydrogen in t-$C_4H_9^+$.

In **VII** the base interacts with two partially charged hydrogens from two methyl groups. An interaction between a base and three partially charged hydrogens from three methyl groups, as shown in **VIII**, seems unlikely since t-$C_4H_9^+$ is a planar species resulting in an adduct structure likely to be sterically congested. To bend the molecular framework of t-$C_4H_9^+$ out of the plane in order that **VIII** be formed should be energetically unfavorable.

The type of interaction, $CH^{\delta+}\cdots B$, which is described by **IV**−**VIII**, has been investigated by Meot-Ner and Deakyne.[39] They investigated the thermochemistry of the association reactions between $(CH_3)_4N^+$ and some n-donors, π-donors, and CH_3Cl by use of PHPMS and *ab initio* calculations. From the *ab initio* calculations they found that in the n-donor complexes the bases attach electrostatically to a cavity created by partially charged hydrogens of three methyl groups rather than interacting with one partially charged hydrogen or with three partially charged hydrogens of one methyl group. From the experimental results they found that the negative enthalpies of association for $(CH_3)_4N^+$ onto the n- and π-donors range between 8 and 10 kcal/mol. With the weak n-donor CH_3Cl they found the interaction to be weaker (6.5 kcal/mol) while a more polar base like $(CH_3)_2CO$ attaches more strongly (14.6 kcal/mol). Since there is no hetero atom in t-$C_4H_9^+$, there must be somewhat less partial charge on the hydrogens compared to that in $(CH_3)_4N^+$. Thus the $CH^{\delta+}\cdots B$ interactions might be expected to be even weaker in t-$C_4H_9^+$ than those in $(CH_3)_4N^+$. As is evident from Table 1 no such weak interactions are thought to be observed in this work. This simplifies the situation since we now can eliminate **IV**−**VIII** in our attempts to assign structures to the observed association adducts.

Ab initio calculations have been carried out in conjunction with the experimental study of the association reactions. Different association adduct structures corresponding to **I**−**VIII** have been attempted for the association reaction of t-$C_4H_9^+$ onto $(CH_3)_2O$. This investigation showed, not surprisingly, that the covalently bound association adduct represents the global minimum on the potential energy surface. The **IV**, **V**, **VI**, and **VIII** structures do not represent minima, however the **III** structure does. The **II** and **VII** structures represent apparent energy plateaus rather than minima, which may indicate that

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Table 3. Theoretically Obtained Thermochemical Data for the Association Reaction of *t*-$C_4H_9^+$ onto Several Bases (B)

		high temperature (**III**)		low temperature (**I**)		
B	PA(B),[a] kcal/mol	$-\Delta H°$,[c] kcal/mol	$-\Delta S°$,[e] cal/(mol·K)	$-\Delta H°$,[c] kcal/mol	$-\Delta S°$,[e] cal/(mol·K)	level of theory
CH_3OH	183.8	14.4	34.9	31.8	46.9	MP2/6-31G(2d,p)
CH_3CN	185.9	*d*	*d*	40.2	43.5	MP2/6-31G(2d,p)
C_2H_5OH	189.1	16.0	34.8	35.6	46.7	MP2/6-31G(d,p)[f]
$(CH_3)_2O$	191.3	*d*	*d*	33.5	50.0	MP2/6-31G(d,p)[f]
$(CH_3)_2CO$	*b*	*b*	*b*	*b*	*b*	
$(C_2H_5)_2O$	*b*	*b*	*b*	*b*	*b*	

[a] From theoretical calculated exchange reactions using PA(*i*-C_4H_8) from ref 33 as the reference. The estimated theoretical uncertainty for PA is ±2 kcal/mol. [b] Not calculated. [c] The estimated theoretical uncertainty for $\Delta H°$ is ±5 kcal/mol. [d] Could not be calculated because of a minor oscillation in the optimized structure. [e] The estimated theoretical uncertainty for the low-temperature $\Delta S°$ values are ±5 cal/(mol·K) and ±15 cal/(mol·K) for the high-temperature $\Delta S°$ values. [f] The MP2/6-31G(2d,p) level of theory has been used for the calculation of PA(C_2H_5OH) and PA($(CH_3)_2O$).

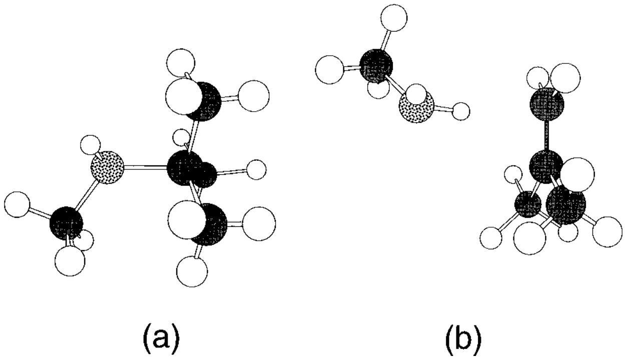

Figure 8. Optimized structures for the covalently bound (a) and electrostatically bound (b) association adducts between *t*-$C_4H_9^+$ and CH_3OH.

they are possible transition states. The **II** and **VII** structures are therefore proposed to be the transition states for the following isomerization reactions:

$$[B{-}H\cdots C_4H_8]^+ \overset{TS_{II}}{\rightleftharpoons} [B\cdots C_4H_9]^+ \overset{TS_{VII}}{\rightleftharpoons} {}^+B{-}C_4H_9 \qquad (10)$$

Since **IV**−**VIII** have already been ruled out as possible adduct structures for the experimentally observed association adducts, and since **II** is suspected to be a possible transition state in the *t*-$C_4H_9^+$ onto $(CH_3)_2O$ system, only **III** is left as a possible electrostatically bound association adduct, if we assume that **II** represents a transition state in all the systems. Since the low-temperature-$\Delta S°$ values all indicate that a covalently bound association adduct is present, the possibility of two electrostatically bound association adducts is ruled out. Therefore the two isomers are, for a given base investigated, proposed to be a covalently bound association adduct, **I**, and an electrostatically bound association adduct, **III**, where the base is protonated and interacts with the π-system in *i*-C_4H_8. Structures corresponding to **I** and **III** have, for some of the systems, been optimized and thermochemical data have been calculated and summarized in Table 3. The optimized adduct structures, **I** and **III**, for *t*-$C_4H_9^+$ onto CH_3OH are presented in Figure 8. As is evident from a comparison of the data in Tables 1 and 3, the experimental $-\Delta H°$ values are in good agreement with the calculated values (within ±5 kcal/mol, except for CH_3CN), which indicates that the use of eq 8 is justified. The calculated low-temperature $-\Delta S°$ values are in relatively poor agreement with the experimental values. This is understandable since the *ab initio* calculations do not adequately consider restriction of internal rotations. This means that the calculated $-\Delta S°$ values for the covalently bound association adducts should be in good agreement with the corresponding estimated values. This is true within ±4 cal/(mol·K). The calculated high-temperature $-\Delta S°$ values are in very poor agreement with the experimental values. This can be explained from the fact that a harmonic oscillator approximation has been used in the frequency calculations, and from the fact that it has been assumed that the vibrational wave function and the rotational wave function can be separated. These approximations are not justified for the electrostatically bound association adducts, **III**, since they contain very low frequency hindered internal rotations. These association reactions will be discussed individually below.

CH_3OH. From Table 1 it is clear that the experimental $-\Delta S°$ value (54.0 cal/(mol·K)) at low temperature is consistent with a covalently bound association adduct, **I**, with the steric congestion contributing ~4 cal/(mol·K) to the $-\Delta S°$ of association. The calculated $-\Delta H°$ value (31.8 kcal/mol) for the low-temperature regime is consistent with the experimental value (29.1 kcal/mol), and thereby supports the proposed covalently bound association adduct, **I**. The calculated $-\Delta H°$ value (14.4 kcal/mol) at high temperature is in very good agreement with the experimentally observed value (15.1 kcal/mol), which is good support for the proposed structure, **III**. The association adduct, **I**, is also the protonation product of *t*-$C_4H_9OCH_3$:

$$t\text{-}C_4H_9^+ + CH_3OH \rightleftharpoons t\text{-}C_4H_9\overset{+}{O}HCH_3 \rightleftharpoons t\text{-}C_4H_9OCH_3 + H^+ \qquad (11)$$

It is also possible to determine the proton affinity of *t*-C_4H_9-OCH_3 from the experimentally determined $\Delta H°$ value (−29.1 kcal/mol) at low temperature. Using $\Delta H_f°(t\text{-}C_4H_9^+) = 170.0$ kcal/mol[33] and $\Delta H_f°(CH_3OH) = -48.1$ kcal/mol[37] gives $\Delta H_f°(t\text{-}C_4H_9O^+HCH_3) = 92.8$ kcal/mol. From this value and $\Delta H_f°(H^+) = 365.7$ kcal/mol[51] and $\Delta H_f°(t\text{-}C_4H_9OCH_3) = -67.8$ kcal/mol[37] we obtain PA(*t*-$C_4H_9OCH_3$) = 205.1 kcal/mol. This value is in excellent agreement with the value calculated from Blake and Jorgensen,[52] who obtained a value of 205.0 kcal/mol, and is in fairly good agreement with the NBS (National Bureau of Standards)[53] value of 202.2 kcal/mol.

CH_3CN. The experimentally observed entropy of association of 45.4 cal/(mol·K) for the low-temperature regime is within the accuracy of the estimated value for a covalently bound association adduct. This indicates a covalently bound association adduct, **I**. The fact that $-\Delta S°$ is only approximately equal to the estimated value suggests very little steric congestion or none at all. This also suggests, not surprisingly, a linear structure with the charge located on the hetero atom, rather than the bent structure with the charge located on the adjacent carbon. The calculated $-\Delta H°$ value (41.1 kcal/mol) for the low-temperature regime is in fair agreement with the experimental value (35.0 kcal/mol), and supports the proposed covalently

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bound association adduct, **I**. Because of a minor oscillation in the optimized electrostatic structure it was not possible to calculate the $-\Delta H°$ value. Attempts to calculate the $-\Delta H°$ value with parts of the adduct frozen gave an absurd result.

C_2H_5OH. The experimentally observed entropy of association of 72.9 cal/(mol•K) for the low-temperature regime suggests a covalently bound association adduct, with a considerable steric congestion, contributing ∼23 cal/(mol•K) to the $-\Delta S°$ of association. This is a larger value than the corresponding value for CH_3OH, which would be expected since the ethyl group is bulkier than the methyl group. The calculated $-\Delta H°$ value (35.6 kcal/mol) for the low-temperature regime is in good agreement with the experimental value (38.6 kcal/mol), and thereby supports the proposed covalently bound association adduct, **I**. The calculated $-\Delta H°$ value (16.0 kcal/mol) at high temperature is within ∼5 kcal/mol of the experimentally observed value (20.4 kcal/mol), which must be considered to be acceptable agreement, since this calculation was done at a lower basis set level (MP2/6-31G(d,p)). The proposed structure, **III**, is therefore likely. The association adduct, **I**, corresponds also in this case to the protonation product of the ether, t-$C_4H_9OC_2H_5$. There is unfortunately no $\Delta H_f°(t\text{-}C_4H_9OC_2H_5)$ value available in the literature, but instead, we have estimated the value as follows. The values of $\Delta H_f°(t\text{-}C_4H_9OCH_3)$ and $\Delta H_f°(t\text{-}C_4H_9OC_2H_5)$ have been estimated using Benson's additivity schemes[36] based on data from ref 37, and the difference has been added to the literature value of $\Delta H_f°(t\text{-}C_4H_9OCH_3)$,[37] which finally gives $\Delta H_f°(t\text{-}C_4H_9OC_2H_5) = -76.0$ kcal/mol. It is then possible to determine the proton affinity of t-$C_4H_9OC_2H_5$ from the experimentally determined $\Delta H°$ value (−38.6 kcal/mol) at low temperature. Using $\Delta H_f°(t\text{-}C_4H_9^+) = 170.0$ kcal/mol[33] and $\Delta H_f°(C_2H_5OH) = -56.2$ kcal/mol[37] gives $\Delta H_f°(t\text{-}C_4H_9O^+HC_2H_5) = 75.2$ kcal/mol. From this value and $\Delta H_f°(H^+) = 367.7$ kcal/mol[51] and the estimated $\Delta H_f°(t\text{-}C_4H_9OC_2H_5) = -76.0$ kcal/mol we obtain $PA(t\text{-}C_4H_9OC_2H_5) = 214.0$ kcal/mol. This value is in very poor agreement with the NBS[53] value of 205.3 kcal/mol. To ensure that this experimentally determined value is reasonable, we have investigated the proton exchange reaction between t-$C_4H_9OCH_3$ and t-$C_4H_9OC_2H_5$, eq 12, since the reaction enthalpy for this process reflects the difference in proton affinity for the two ethers.

$$t\text{-}C_4H_9O^+HCH_3 + t\text{-}C_4H_9OC_2H_5 \rightleftharpoons t\text{-}C_4H_9OCH_3 + t\text{-}C_4H_9O^+HC_2H_5 \quad (12)$$

Values of $\Delta H° = -10.7$ kcal/mol and $\Delta S° = -16.6$ cal/(mol•K) were extracted from the van't Hoff plot. From the association reactions with t-$C_4H_9^+$ we have determined a difference of 8.9 kcal/mol in proton affinity for the two ethers, which is in fair agreement with the value of 10.7 kcal/mol from the investigation of the exchange reaction. In fact the value based on the clustering energetics is likely in error due to the underestimation of $\Delta H_f°(t\text{-}C_4H_9OC_2H_5)$. Values of $\Delta G°$ for the proton exchange reactions between NH_3 and t-$C_4H_9OCH_3$ or t-$C_4H_9OC_2H_5$ are also available in the literature.[53] The difference in these values reflects the difference in gas-phase basicity of the two ethers, which combined with the $\Delta S°$ value from the exchange reaction investigated in the present work gives a difference in proton affinity of 9.9 kcal/mol, a value in excellent agreement with the difference in proton affinity obtained in the present work. A potential energy surface for the association reaction is proposed in Figure 9.

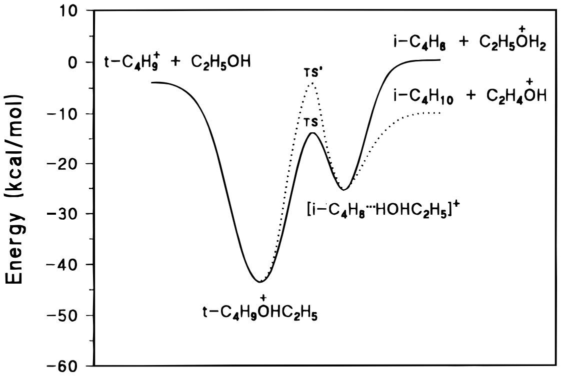

Figure 9. Potential energy profile for the association reaction of t-$C_4H_9^+$ onto C_2H_5OH. The energy of the TS is arbitrary. The energy for i-$C_4H_{10} + C_2H_4OH^+$ is calculated from values taken from ref 51.

$(CH_3)_2O$. In this case the experimentally observed entropy of association of 62.1 cal/(mol•K) for the low-temperature regime also suggests a covalently bound association adduct. The steric congestion here contributes ∼12 cal/(mol•K) to the $-\Delta S°$ of association, a value which should be, and is, larger than the corresponding value for CH_3OH, since we now have two methyl groups instead of one. The calculated $-\Delta H°$ value (34.3 kcal/mol) for the low-temperature regime supports the experimental value (33.2 kcal/mol), and thereby lends credence to the proposed covalently bound association adduct, **I**. Because of a minor oscillation in the optimized electrostatic structure it was not possible to calculate the $-\Delta H°$ value. Attempts to calculate the $-\Delta H°$ value with parts of the adduct frozen gave an absurd result.

$(CH_3)_2CO$. Again the experimentally observed entropy of association of 54.4 cal/(mol•K) for the low-temperature regime suggests a covalently bound association adduct, with a steric congestion contributing ∼9 cal/(mol•K) to the $-\Delta S°$ of association. Due to the size of the association adduct, no theoretical calculations were performed.

$(C_2H_5)_2O$. Finally the experimentally observed entropy of association of 86.4 cal/(mol•K) for the low-temperature regime is here ∼36 cal/(mol•K) higher than the estimated value. This suggests a covalently bound association adduct with a considerable sterical congestion. Due to the size of the association adduct no theoretical calculations were performed.

Wojtyniak and Stone[46] have investigated the binding of $(CH_3)_3Si^+$ to oxygen in aromatic bases and found a linear correlation between the $(CH_3)_3Si^+$ affinities and the proton affinities. The slope of the correlation lines is a measure of the sensitivity of binding energy to changes in the structure of the base remote from the binding site for $(CH_3)_3Si^+$ relative to H^+.[46]

In Figure 10 $(CH_3)_3C^+$ affinities (from the present work) and $(CH_3)_3Si^+$ affinities (from ref 46) are plotted against proton affinities. When using the low-temperature values for CH_3OH, $(CH_3)_2O$, and $(CH_3)_2CO$ a linear correlation is observed between the $(CH_3)_3C^+$ affinities and the proton affinities. The slope of the correlation line is comparable to the corresponding correlation line for $(CH_3)_3Si^+$. The plot shows that $(CH_3)_3Si^+$ affinities are ∼10 kcal/mol greater than the $(CH_3)_3C^+$ affinities, which is expected because of the shorter Si−O distance in the silicon adduct. Since CH_3CN is a nitrogen base, it is not expected to have a comparable correlation with the oxygen bases. However, C_2H_5OH and $(C_2H_5)_2O$ each show an apparently anomalous behavior. It could be argued that these bases might be expected to show anomalous behavior since they both have ethyl groups attached to the oxygen which could give rise to a possible additional hydride bridging interaction, not found in species other than those containing ethyl groups. This extra interaction then results in the apparent additional stabilization. From an investigation of the MIKES spectra, which were done on a modified VG 70-70 mass spectrometer[33] whose geometry

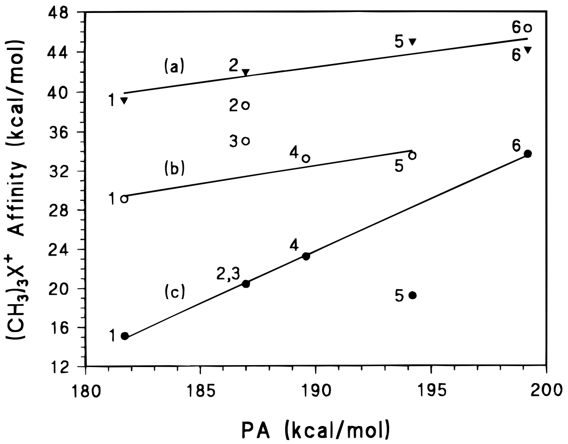

Figure 10. The correlation between proton affinities and $(CH_3)_3X^+$ affinities: (a) X = Si, from ref 46, (b) X = C, low-temperature regime, present work, (c) X = C, high-temperature regime, present work; (1) CH_3OH, (2) C_2H_5OH, (3) CH_3CN, (4) $(CH_3)_2O$, (5) $(CH_3)_2CO$, (6) $(C_2H_5)_2O$.

was reversed to provide a B-E instrument, it was revealed that all of the association adducts of C_2H_5OH and $(C_2H_5)_2O$ lose i-C_4H_{10} as one of the dominant reaction channels, whereas all of the other association adducts always have this reaction channel as a much less significant if not non-existent fragmentation. These observations are consistent with the work done by Monteiro *et al.*,[48] who studied the dissociation of metastable protonated alkyl ethers and found that these species lose i-C_4H_8, i-C_4H_{10}, and ROH in different proportions dependent on the alkyl ether studied.

As is evident from Figure 10, there is an even more distinct correlation between the high-temperature $(CH_3)_3C^+$ affinities and the proton affinities. All values except that for $(CH_3)_2CO$ fall on the correlation line. The anomalous behavior of $(CH_3)_2CO$ can be explained from the fact that the protonated $(CH_3)_2CO$ differs significantly from the other protonated bases interacting with i-C_4H_8, since the charge is formally not located on the hetero atom, but rather on the adjacent carbon. This leaves two possibilities for an electrostatically bound association adduct: (i) a structure where the proton located on the oxygen is interacting with the π-system in i-C_4H_8, $[i\text{-}C_4H_8\cdots H-OC(CH_3)_2]^+$, and (ii) a structure were the carbonium center is interacting with the π-system in i-C_4H_8, $[i\text{-}C_4H_8\cdots COH(CH_3)_2]^+$. The distinct correlation between the proton affinities and the enthalpy of association at high temperature shows that the reaction enthalpies of i-C_4H_8 clustering onto the protonated base, eq 13, in general are approximately the same (~25 kcal/mol) for the systems investigated.

$$i\text{-}C_4H_8 + BH^+ \rightleftharpoons [i\text{-}C_4H_8\cdots BH]^+ \qquad (13)$$

Conclusion

As is evident from the data presented herein, the association adducts of t-$C_4H_9^+$ onto a given base investigated can exist in two isomeric forms dependent on the temperature: (i) a low-temperature, covalently bound isomer characterized by larger $-\Delta H°$ and $-\Delta S°$ values, which at higher temperatures can shift to (ii) an electrostatically bound isomer of lower $-\Delta H°$ and $-\Delta S°$ values.

Negative association enthalpies from 29 to 46 kcal/mol and negative association entropies from 45 to 86 cal/(mol·K) are observed for the low-temperature regime. These values are consistent with a covalently bound isomer, **I**, with approximately tetrahedral geometry at the central carbon of the *tert*-butyl group. The restriction of the rotational motions of the *tert*-butyl group and the methyl groups in the *tert*-butyl substituent, as well as those about bonds in the neutral participants gives rise to the large entropy changes for the association reactions at low temperature. This makes the covalent form relatively straightforward to identify. From the low-temperature data it was possible to determine the proton affinities of t-$C_4H_9OCH_3$ (205.1 kcal/mol) and t-$C_4H_9OC_2H_5$ (214.0 kcal/mol). Both are in excellent agreement with literature values. A linear correlation has been found between the t-$C_4H_9^+$ affinities and the proton affinities for the following oxygen bases for the low-temperature regime, CH_3OH, $(CH_3)_2O$, and $(CH_3)_2CO$, whereas C_2H_5OH and $(C_2H_5)_2O$ show an unexpected enhancement in enthalpy of association, possibly due to an additional hydride bridging interaction.

Negative association enthalpies from 15 to 34 kcal/mol and negative association entropies from 21 to 52 cal/(mol·K) are observed for the high-temperature regime. These values are consistent with an electrostatically bound association adduct, **III**, where the base is protonated and interacts with the π-system in i-C_4H_8. A linear correlation was found between the t-$C_4H_9^+$ affinities and the proton affinities for all the bases investigated except for $(CH_3)_2CO$, which showed an understandably anomalous behavior. This correlation indicates that the binding enthalpy between i-C_4H_8 and BH^+ in general is ~25 kcal/mol for the systems investigated.

Ab initio calculations carried out in conjunction with the experimental study of some of these association reactions support the proposed structures, **I** and **III**. The theoretically calculated $\Delta H°$ values are within ~5 kcal/mol (except for CH_3CN at low temperature) of the experimental values; the theoretically calculated proton affinity values are within ~2 kcal/mol of the experimental values, and the theoretically calculated $\Delta S°$ values for the low-temperature regime are within ~5 cal/(mol·K) of the experimental values. This is taken to be acceptable agreement considering the levels of theory used. *Ab initio* calculations carried out for t-$C_4H_9^+$ onto $(CH_3)_2O$ revealed two energy plateaus when attempting to optimize different electrostatically bound adduct structures. Structures corresponding to these energy plateaus are proposed to be possible transition states characterized by unconventional ionic hydrogen bonds: (i) a structure, **II**, where the base interacts with a nonclassical form of t-$C_4H_9^+$, and (ii) a structure, **VII**, where the base interacts with two partially charged hydrogens from two methyl groups in t-$C_4H_9^+$.

As is evident from the present work, the use of the PHPMS technique is an effective way of obtaining thermochemical data for association reactions, eq 7, and exchange reactions, eq 6, in the gas phase. We have furthermore illustrated how powerful a tool the examination of the thermochemistry of the association of an ion with a neutral molecule is for the inference of gross structural features of an ion−molecule adduct.

Future work will focus on similar investigations of association adducts between bases and species containing one or more conjugated π-systems or aromatic compounds.

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