The *tert*-Butyl Ion Heat of Formation and the Isobutene Proton Affinity

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A new value of the *tert*-butyl ion heat of formation has been measured by dissociative ionization of *tert*-butyl iodide using the photoelectron photoion coincidence technique. The derived $\Delta H_f{}^\circ{}_0(\text{t-C}_4\text{H}_9{}^+)$ of 734 kJ/mol and $\Delta H_f{}^\circ{}_{298}(\text{t-C}_4\text{H}_9{}^+)$ of 711 kJ/mol is 20 kJ/mol higher than previous experimental measurements,[1-4] but agrees within 1 kJ/mol with a recent theoretical *ab initio* calculation.[5] The derived proton affinity for isobutene is thus 802 kJ/mol at 298 K.

The proton affinity (PA) of a molecule, A, is defined through the enthalpy of the following reaction:

$$\text{A} + \text{H}^+ \rightarrow \text{AH}^+ \qquad \text{PA} = -\Delta H^\circ \tag{1}$$

The PA is thus related to the heats of formation by

$$\text{PA} = -\Delta H_f{}^\circ(\text{AH}^+) + \Delta H_f{}^\circ(\text{H}^+) + \Delta H_f{}^\circ(\text{A}) \tag{2}$$

While absolute heats of formation and PAs are generally difficult to measure, relative proton affinities can be established from gas-phase equilibria with great precision through reactions such as

$$\text{AH}^+ + \text{N} \Leftrightarrow \text{A} + \text{NH}^+ \tag{3}$$

A large number of such studies have been carried out by ion cyclotron resonance (ICR),[6] high-pressure mass spectrometry,[7-9] and flowing afterglow (FA) studies.[10] Because of the high precision of these measurements, it is possible to derive accurate heats of formation of neutrals and ions that are difficult to determine by other methods. In 1984 and 1988 Lias *et al.*[3,4] published a large compilation of the derived proton affinities based on the measurements of relative proton affinities in the literature. Absolute values were obtained by fixing the scale to various "known" proton affinities. The PA scale is thus anchored by several standards, among them the PA of isobutene. Attachment of a proton to isobutene yields

$$(\text{CH}_3)_2\text{C}{=}\text{CH}_2 + \text{H}^+ \rightarrow (\text{CH}_3)_3\text{C}^+ \tag{4}$$

Smith and Radom[5] recently evaluated the proton affinities of over 30 compounds by *ab initio* molecular orbital calculations. While they found that the majority of their values agreed with those in the Lias compilation, several values differed by a considerable amount. The most dramatic discrepancy was in the PA value of isobutene, which they calculated to be 802.1 kJ/mol (at 298 K) compared to 820 kJ/mol.[3] Furthermore, Smith and Radom traced this discrepancy to the heat of formation of the *tert*-butyl ion, which they calculated to be 714.4 kJ/mol (at 298 K) compared to the literature value of 694 kJ/mol. Interstingly, Szulejko and McMahon have recently reevaluated the PA scale by extensive ion equilibrium studies on 80 molecules, including isobutene. They concluded that "the value of $\Delta H_f{}^\circ$ for the *tert*-butyl cation must be significantly higher than that derived from appearance energy measurements...".[9] Until now, the *tert*-butyl cation heat of formation has been based on (a) the dissociative photoionization onset from several precursor molecules[1,2] and (b) the measured ionization potential of the *tert*-butyl radical[11,12] and the neutral *tert*-butyl heat of formation of 46.2 kJ/mol.[4] However, the latter method gave the low value only if the adiabatic IP of 6.7 eV obtained from a PES study[12] was used, rather than the vertical IP or Lossing's[11] energy selected electron impact onset of 6.93 eV.

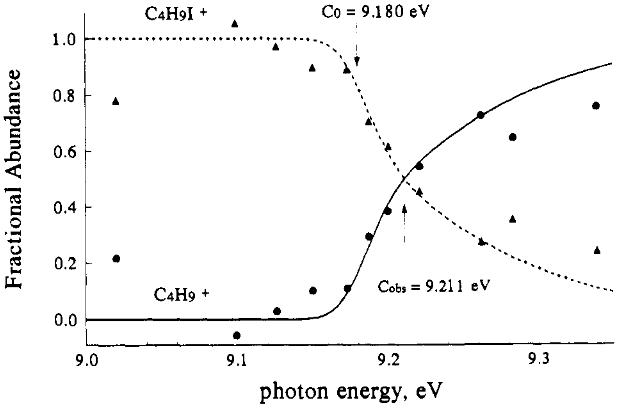

Figure 1. The 0 K breakdown diagram of *tert*-butyl iodide ions in the vicinity of the I atom loss channel. The points are experimental PEPICO results, while the solid and dashed lines are calculated by convoluting ideal step functions with the electron energy analyzer function. The derived 0 K dissociation limit is 9.180 ± 0.015 eV.

Although the *tert*-butyl ion is particularly stable and thus appears as a frequent product in ion–molecule reactions, its heat of formation has been difficult to establish. In order to determine the *tert*-butyl ion heat of formation from the dissociative photoionization of $(\text{CH}_3)_3\text{CX}$ via

$$(\text{CH}_3)_3\text{CX} + h\nu \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{X} \tag{5}$$

the system must meet a number of requirements. The neutral $(\text{CH}_3)_3\text{CX}$ must have a known heat of formation, the parent ion must be stable at low ionization energies, reaction 3 must be the lowest energy dissociation process, the reaction must be rapid, and finally, the reaction must have no reverse activation energy. The only precursor molecule that appears to meet all these requirements is *tert*-butyl iodide.

In this study we have used our photoelectron photoion coincidence (PEPICO) technique[13] to measure the dissociative photoionization onset of *tert*-butyl iodide cooled in a supersonic molecular beam. The experiment consists of monitoring the intensity of the parent and daughter ions as a function of the photon energy. A plot of fractional abundance of the parent and daughter ion as a function of the ion internal energy, called a breakdown diagram, is shown in Figure 1. The data were obtained by integrating the mass peaks in a PEPICO ion time of flight spectrum. Data were collected with a room temperature and a molecular beam sample. By a method previously described,[13] it was established from the TOF distribution that the molecular beam consisted of 75% cold and 25% warm sample. The contribution from the warm background gas was thus subtracted from spectra taken with the molecular beam. The resulting pure cold breakdown diagram is shown in Figure 1. Because of the

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Table I. *tert*-Butyl Ion Heat of Formation and Isobutene Proton Affinity (kJ/mol)[a]

	derived from this study		other values
	0 K	298 K[b]	298 K[b]
$\Delta H_f(C_4H_9^+)$	734 ± 3.6	711 ± 3.6	695[c] 705[d] 714.4[e]
PA(isobutene)	798 ± 3.6	802 ± 3.6	820[f] 802.1[d] 802.1[g]

[a] The *tert*-butyl ion heat of formation and the isobutene proton affinity were derived using the following supplementary heats of formation: $\Delta H_f(C_4H_9I) = -44.5$ (0 K), -72.0 ± 3.3 (298 K) from ref 22; $\Delta H_f(C_4H_8) = 4.4$ (0 K), -16.9 ± 0.9 (298 K) from ref 22; $\Delta H_f(I) = 107.2$ (0 K), 106.8 (298 K) both from ref 23; $\Delta H_f(H^+) = 1528$ (0 K), 1530.0 (298 K) both from ref 4. The 0 K values with no references were converted from the 298 K values in this study. [b] The electron is assumed to remain at 0 K. To compare with values in which the electron is treated as a normal particle at 298 K, add $(5/2)RT = 6.2$ kJ/mol to the 298 K heats of formation. [c] References 2 and 4. [d] Reference 24. [e] Reference 5. [f] Reference 3. [g] Reference 9.

molecular beam cooling effect, the crossover energy is shifted from about 9.05 eV in the warm sample to 9.18 eV.

The ideal 0 K breakdown diagram would exhibit sharp steps (down for parent ion and up for daughter ion) at the 0 K dissociation limit. The experimental spectrum tails toward the high-energy side. This is a result of the combined photon and electron energy resolution of 25 meV and the imperfect suppression of energetic electrons by the steradiancy electron energy analyzer.[14] The solid and dashed lines are the calculated breakdown diagram in which the instrumental resolution function is convoluted with the ideal step function. From this analysis, we conclude that the 0 K dissociative photoionization limit of *tert*-butyl iodide ion is 9.180 ± 0.015 eV. This can be compared to the previously measured value of 8.98 eV which was measured with warm samples.[1,15]

Reaction 5 with X = I can then be used to calculate a 0 K heat of formation of the *tert*-butyl ion, and with that, the isobutene proton affinity (reaction 4). These derived values are listed in Table I. The literature heats of formation at 298 K for isobutene and *tert*-butyl iodide were converted to 0 K values by the usual methods.[2,16,17] For this purpose vibrational frequencies for isobutene were taken from Shimanouchi[18] while vibrational frequencies obtained from *ab initio* molecular orbital calculations with the Gaussian 90 program with a HF/6-31G* basis set[19] were used for the *tert*-butyl iodide. Similarly, we converted the 0 K heat of formation to 298 K using calculated vibrational frequencies for the *tert*-butyl ion.[19]

It is evident that the new value of the isobutene proton affinity agrees to within 1 kJ/mol with the calculated *ab initio* value[5] as well as the suggested value of Szulejko and McMahon.[9] It is thus 18 kJ/mol less than the previously measured values. The major uncertainties in our determination of the *tert*-butyl ion heat of formation are in the *tert*-butyl iodide heat of formation, which is listed as ±3.3 kJ/mol, and in the assumption that there is no reverse activation energy. The latter assumption was tested by measuring the average kinetic energy released, ⟨KER⟩. At an excess energy of 0.1 eV, the measured ⟨KER⟩ was just 3 meV, which is precisely the value expected on the basis of a statistical product energy distribution and no reverse barrier.[20]

It is interesting that the raising of the *tert*-butyl ion heat of formation to 712 kJ/mol is accompanied by a similar proposed increase in the neutral *tert*-butyl radical heat of formation (51.3 kJ/mol).[21] With these values established, we predict a *tert*-butyl radical ionization potential of 6.85 eV, which is close to Houle and Beauchamp's vertical IP from PES (6.92 eV) and Lossing's reported onset of 6.92 eV. However, it is considerably higher than the reported adiabatic IP of 6.7 eV. Studies with cold *tert*-butyl radicals are needed to firmly establish the ionization potential of this free radical.

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