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(50) NOTE ADDED IN PROOF. It has recently been reported (de Tacconi, N. R.; Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 467–473) that dissociation of the dimethylbenzimidazole group of aquocobalamin occurs with a pH-independent rate constant of ~0.1 $s^{-1}$ at low pH values. Further experimental work is required to explain the apparent difference in the behavior of aquocobalamin and cyanocobalamin and the unexpectedly small difference between the pH-independent rate constants of 0.1 $s^{-1}$ for aquocobalamin and 0.042 $s^{-1}$ for cyanocobalamin; conclusions regarding the mechanism of DMBz dissociation must be regarded with reservation until these differences are explained.

# Heat of Formation for *tert*-Butyl Cation in the Gas Phase

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**Abstract:** The appearance energies of $C_4H_9^+$ ions formed from isobutane and the *tert*-butyl halides have been measured by photoionization mass spectrometry. A heat of formation of 162.1 ± 0.8 kcal $mol^{-1}$ has been derived for the *tert*-butyl cation in the gas phase. This result is discussed in terms of its use as a gas-phase proton affinity standard. A value of 7.6 ± 1.5 kcal $mol^{-1}$ has been obtained for the *tert*-butyl radical heat of formation.

## Introduction

In a recent photoelectron spectroscopic study of alkyl radicals,[1] it was proposed that the heat of formation for the *tert*-butyl cation is 162.9 kcal $mol^{-1}$, considerably less than the currently accepted value.[2] Since the proton affinity (PA) of isobutene is used as a reference for determining absolute proton affinities,[3-5] it is important that this standard, which is derived from $\Delta H_f((CH_3)_3C^+)$, be firmly established.

Previous estimates of the heat of formation of *tert*-butyl cation[2,3] have been derived from an ionization energy of the radical[6] which has since been shown[1,7] to be a vertical rather than an adiabatic value. In addition, the *tert*-butyl radical heat of formation used in the thermochemical calculation is not accurately known, with values ranging from 6.8 to 12.9 kcal $mol^{-1}$.[8-11] Houle and Beauchamp[1] have chosen Benson's value of 8.4 kcal $mol^{-1}$ [9] which they support with experimental ionic equilibria data for benzyl cation reacting with *tert*-butyl chloride and *tert*-butyl bromide (loc. cit. ref 1). However, the combined uncertainty of ≥ ±3 kcal $mol^{-1}$ in the auxiliary thermochemical data used in the calculations does not satisfactorily resolve the question surrounding the heat of formation for *tert*-butyl radical. Moreover, the recent experiments of Rossi and Golden,[12] which propose an increase of 2 kcal $mol^{-1}$ in the heat of formation for benzyl radical, and hence benzyl cation, cast further doubt on the *tert*-butyl radical heat of formation recommended by Houle and Beauchamp.[1] Ausloos and Lias[4,13] recognized the uncertainty in this direct method of calculating $\Delta H_f((CH_3)_3C^+)$ and preferred to base their PA calculations on a value of 168.2 kcal $mol^{-1}$ derived from an appearance energy measurement for $C_4H_9^+$ from neopentane.[14]

In an attempt to clarify this situation, we have calculated a heat of formation for *tert*-butyl cation in the gas phase from several $C_4H_9^+$ appearance energy measurements using a photoionization mass spectrometer. Previous experience has shown that we are able to determine accurate heats of formation for ionic species,[15-18] provided that reliable supplementary thermochemical data are available. The series of compounds studied in the present work ($(CH_3)_3X$; X = Cl, Br, I, H) all have well-characterized heats of formation[19] as do the neutral species[20] ejected in the ionization–fragmentation process.

## Experimental Section

The photoionization mass spectrometer has been described in detail elsewhere.[21] The photon source used in the present studies was the molecular hydrogen pseudocontinuum with an energy dispersion of 1.25 Å FWHM. All experiments were performed at ambient temperature (296 K). The compounds used were of high purity and showed no impurities of significance in their mass spectra.

## Results and Discussion

The photoion yield curves corresponding to formation of $(CH_3)_3C^+$ from the four precursor molecules studied are shown in Figure 1, with the ion appearance energies, heats of formation, and auxiliary thermochemical data being summarized in Table I. The observed $C_4H_9^+$ ions may be inferred to have the *tert*-butyl cation structure as the calculated ionic heats of formation are all too low to be equated with other isomeric structures.[6]

For *tert*-butyl chloride and *tert*-butyl bromide, where no parent ions are observed, the ionization energy and corresponding $C_4H_9^+$ appearance energy are the same within experimental error. Because the fragmentation processes occur subsequent to initial ionization of the neutral precursor, the calculated $C_4H_9^+$ heats of formation will only represent an upper limit to $\Delta H_f((CH_3)_3C^+)$. This is also the case for *tert*-butyl iodide, even though there is a molecular ion observed in the mass spectrometer. The heat of formation calculated from the isobutane results should be representative of $\Delta H_f((CH_3)_3C^+)$ since the ionization energy is less than the appearance energy. Any excess energy involved in the process is expected to be negligible because of the small kinetic energy release (~0.007 eV)[22] associated with the corresponding metastable fragmentation.

As a consequence of the rapid fragmentation process following ionization of the *tert*-butyl halides, it is expected that there will be no observable kinetic shift. This is supported by the well-defined thresholds of the three photoion yield curves (Figure 1). The low-energy tail of each curve is consistent with the extent of expected hot band structure, i.e., ionization and subsequent fragmentation of thermally excited neutral precursor molecules. Following the theoretical studies of Chupka[23] and Guyon and Berkowitz,[24] a linear extrapolation of the ob-

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**Table I.** Thermochemistry for the Reaction $t$-BuX + $h\nu \rightarrow t\text{-Bu}^+ + X + e^-$

| X | $I(t\text{-BuX})^a$ | $A(t\text{-Bu}^+)^a$ | $\Delta H_f^b$ $t$-BuX | $\Delta H_f^b$ X | $\Delta H_f^b$ $t\text{-Bu}^+$ |
|---|---|---|---|---|---|
| Cl | 10.51 ± 0.02[c] | 10.51 ± 0.01[e] | −43.7 ± 0.6[f] | 28.992[h] | <169.7 |
| Br | 9.89 ± 0.03[d] | 9.85 ± 0.01[e] | −31.88 ± 0.30[f] | 26.735[h] | <168.5 |
| I | 8.98 ± 0.01[e] | 8.98 ± 0.01[e] | −17.4 ± 0.6[f] | 25.517[h] | <164.2 |
| H | <10.50[d,e] | 10.68 ± 0.03[e] | −32.07 ± 0.15[g] | 52.103[h] | 162.1 |

[a] eV. [b] kcal $\text{mol}^{-1}$. [c] PES value, this work. [d] Ref 2. [e] PI value, this work. [f] Ref 19. [g] Ref 29. [h] Ref 20.

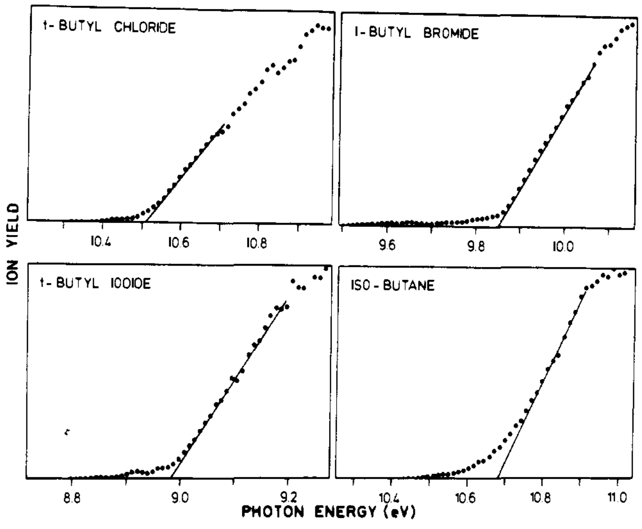

Figure 1.

served threshold curve should thus give a precise measure of the 298 K appearance energy. In the case of isobutane, the slower fragmentation process leads to some additional curvature of the photoion yield curve (Figure 1) and hence to a greater uncertainty in the appearance energy. However, it is unlikely that the 298 K appearance energy is outside the quoted error range[25] (Table I).

The calculated value of 162.1 ± 0.8 kcal $\text{mol}^{-1}$ for $\Delta H_f((CH_3)_3C^+)$ from the present work is in excellent agreement with that of Houle and Beauchamp[1] (162.9 ± 1.2 kcal $\text{mol}^{-1}$), indicating that the previously accepted values[2-4] are indeed too high. When the present calculated value is combined with the radical adiabatic ionization energy (6.70 ± 0.03 eV),[1] a heat of formation of 7.6 ± 1.5 kcal $\text{mol}^{-1}$ is derived for the *tert*-butyl radical. This is in good agreement with the lower reported values[8-10] for this quantity but differs markedly from the more recent determination of 11.7-12.9 kcal $\text{mol}^{-1}$.[11] It may be that the observed ionization energy is higher than the quoted adiabatic value, although this is not supported by the experimental photoelectron spectra of the *tert*-butyl radical.[1,7] In view of this, the validity of the proposed higher radical heat of formation[11] must be questioned.

As a consequence of the alteration to $\Delta H_f((CH_3)_3C^+)$, the proton affinity of isobutene should be revised upward by an equivalent amount; this leads to a value of 199.3 kcal $\text{mol}^{-1}$ for PA(isobutene).[26] Combination of the enthalpy change for proton transfer from $(CH_3)_3C^+$ to $CH_3COCH_3$ (−1.5 kcal $\text{mol}^{-1}$)[13] and the enthalpy change for proton transfer from $(CH_3COCH_3)H^+$ to $NH_3$ (−8.4 kcal $\text{mol}^{-1}$)[27] with PA(isobutene) gives a value for PA ($NH_3$) of 209.2 kcal $\text{mol}^{-1}$. This result compares favorably with the value of PA ($NH_3$) = 208.7 kcal $\text{mol}^{-1}$ obtained from the known enthalpy change for proton transfer from $CH_3CO^+$ to $NH_3$ (−6.4 kcal $\text{mol}^{-1}$)[28] and a calculated proton affinity for ketene (202.3 kcal $\text{mol}^{-1}$),[4] in further support of the present experimental value (162.1 ± 0.8 kcal $\text{mol}^{-1}$) for the heat of formation of *tert*-butyl cation in the gas phase.

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