

- (1975); (c) E. Koerner von Gustorf, M. C. Henry, and D. J. McAdoo, *Justus Liebig's Ann. Chem.*, **707**, 190 (1967); (d) S. D. Ittel, *Inorg. Chem.*, **16**, 2589 (1977), and references cited therein; (e) W. Partenheimer, *J. Am. Chem. Soc.*, **98**, 2779 (1976), and references cited therein.
- (19) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 2775 (1967).
- (20) J. R. Norton, private communication; cf. (a) J. Okrasinski and J. R. Norton, *J. Am. Chem. Soc.*, **99**, 295 (1977); (b) J. Evans and J. R. Norton, *ibid.*, **96**, 7577 (1974).
- (21) S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Grynkeiwich, T. J. Marks, D. L. Tipton, and B. R. Whittlesey, *J. Am. Chem. Soc.*, **99**, 7155 (1977), and references cited therein.
- (22) See, for example, J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975).
- (23) G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91**, 3341 (1969).
- (24) (a) H. G. Kuivila, *Acc. Chem. Res.*, **1**, 299 (1968). (b) C. Walling, J. H. Cooley, A. A. Ponnaras, and E. J. Racah, *J. Am. Chem. Soc.*, **88**, 5361 (1966). (c) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968). (d) The rate constant for transfer of hydrogen from NaBH<sub>4</sub> to a number of organic radicals has been found to be several orders of magnitude slower than transfer from (*n*-Bu)<sub>3</sub>SnH; cf. J. T. Groves and S. Kittisopikul, *Tetrahedron Lett.*, 4291 (1977).
- (25) See, for example, (a) D. M. Singleton and J. K. Kochi, *J. Am. Chem. Soc.*, **89**, 6547 (1967); (b) J. Halpern and J. P. Maher, *ibid.*, **86**, 2311 (1964); (c) P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).
- (26) (a) A. Streitwieser, J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron Lett.*, 338 (1959); (b) H. J. Dauben and L. L. McKoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).
- (27) (a) J. F. Garst, R. D. Roberts, and J. A. Pacifici, *J. Am. Chem. Soc.*, **99**, 3528 (1977), and references cited therein; (b) P. J. Krusic, P. J. Fagan, and J. San Filippo, Jr., *ibid.*, **99**, 252 (1977); (c) B. W. Bangert, R. P. Beatty, J. K. Kouba, and S. S. Wreford, *J. Org. Chem.*, **42**, 3247 (1977).
- (28) (a) C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, **94**, 6059 (1972); (b) M. Julia, *Pure Appl. Chem.*, **15**, 167 (1967); (c) M. Julia, *Acc. Chem. Res.*, **4**, 386 (1971); (d) D. Lai, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).
- (29) See, for example, (a) A. L. J. Beckwith, I. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, **96**, 1613 (1974); (b) A. L. J. Beckwith and W. B. Gara, *J. Chem. Soc., Perkin Trans. 2*, 796 (1975); (c) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).
- (30) For similar complexes, see R. Tsumura and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **38**, 1901 (1965).
- (31) For a discussion of the use of **29** in trapping radicals formed during reduction of alkylmercuric halides by sodium borohydride, see C. L. Hill and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 870 (1974).
- (32) B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 7024 (1976).
- (33) (a) H. Schuh, E. J. Hamilton, Jr., H. Paul, and H. Fischer, *Helv. Chim. Acta*, **57**, 2011 (1974); (b) M. J. Perkins and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 297 (1974).
- (34) G. Brunton, H. C. McBay, and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 4447 (1977).
- (35) (a) H. G. Kuivila and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **88**, 571 (1966); (b) E. J. Walsh, Jr., and H. G. Kuivila, *ibid.*, **88**, 576 (1966).
- (36) P. Beak and S. W. Moje, *J. Org. Chem.*, **39**, 1320 (1974).
- (37) J. E. Ellis, S. G. Hentges, D. G. Kalina, and G. P. Hagen, *J. Organomet. Chem.*, **97**, 79 (1975).
- (38) S. H. Babcock, *Inorg. Synth.*, **1**, 10 (1939).
- (39) H. H. Horhold, G. Drefall, and P. Hinderson, *Z. Chem.*, **7**, 459 (1967).
- (40) W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958).
- (41) W. E. Truce and J. J. Breiter, *J. Am. Chem. Soc.*, **84**, 1623 (1962).
- (42) J. S. Meek and J. W. Rowe, *J. Am. Chem. Soc.*, **77**, 6675 (1955).
- (43) G. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).
- (44) H. E. Carter, R. L. Frank, and H. W. Johnston, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 167.
- (45) M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967.
- (46) C. D. Beard, K. Baum, and V. Grakaukas, *J. Org. Chem.*, **38**, 3675 (1975).
- (47) J. K. Ruff, *Inorg. Synth.*, **15**, 84 (1974).
- (48) J. Colonge, G. Descotes, and G. Poilane, *Bull. Soc. Chim. Fr.*, 408 (1959).
- (49) A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Lett.*, 2251 (1974).

## Structures of Butyl Ions Formed by Electron Impact Ionization of Isomeric Butyl Halides and Alkanes

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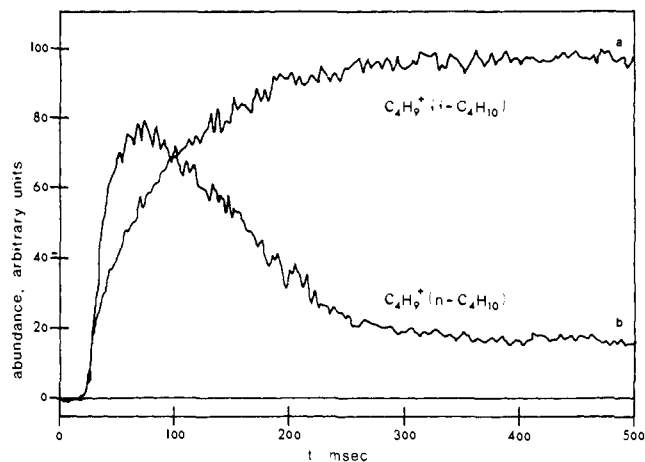
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**Abstract:** Using a pulsed ion cyclotron resonance (ICR) spectrometer, it is demonstrated that at pressures of about 10<sup>-6</sup> Torr and at observation times ranging from 10<sup>-3</sup> to 0.5 s. isobutane, neopentane, 2,2-dimethylbutane, isobutyl halides, and *tert*-butyl halides form C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions having the tertiary structure. In *n*-alkanes, 2-methylbutane, 3-methylpentane, *n*-butyl halides, and *sec*-butyl halides, both *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions are observed, the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions surviving without rearrangement for at least 0.1 s. However, in the case of the halides, a collision-induced isomerization of the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> to the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions occurs. The efficiency of this process increases with the basicity of the alkyl halide. Radiolysis experiments carried out at atmospheric pressures indicate, in agreement with ICR and solution experiments, that at times as short as 10<sup>-10</sup> s the majority of the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions from isobutyl bromide rearrange to the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> structure. On the other hand, in the radiolysis of both *n*-hexane and 3-methylpentane, the abundance of *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> relative to *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> is substantially smaller than that observed in the ICR experiments, and decreases with decreasing collision interval. It is suggested that about 90% of the *i*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> can rearrange to *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> by simple 1,2-hydride shift without involving secondary or protonated methylcyclopropane structures as intermediates.

### Introduction

More than a decade ago, Munson<sup>1,2</sup> demonstrated that *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions can retain their structure in the ion source of a mass spectrometer for up to 10<sup>-6</sup> s. In a more recent collisional activation study by Dymerski and McLafferty,<sup>3</sup> a similar conclusion was reached. In addition, the suggestion was made that *i*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions originating from the electron impact induced fragmentation of *i*-C<sub>4</sub>H<sub>9</sub>Br isomerize mainly to the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> structure within 10<sup>-6</sup> s. As pointed out by these authors, solution isomerization studies<sup>4</sup> as well as the interpretation of isomerization mechanisms occurring in the radiolysis of alkanes<sup>5</sup> lead to a different conclusion, namely, that isobutyl ions rearrange mainly to the tertiary

structure. A new attempt to identify the structures of butyl ions was made using a pulsed ion cyclotron resonance spectrometer (ICR) which permits the observation of ions at times as long as seconds after their formation. The approach was the same as that employed in a recent ICR examination of C<sub>7</sub>H<sub>7</sub><sup>+</sup> structures.<sup>6</sup> A previous examination of the C<sub>4</sub>H<sub>9</sub><sup>+</sup> structures<sup>7</sup> using an ICR operating in the continuous mode was thought to give inconclusive results because no distinction could be made between structurally different ions and structurally similar ions containing different amounts of internal energy. In order to circumvent internal energy effects, the present study mainly examines C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions which have undergone several unreactive collisions prior to reaction. In addition we report



**Figure 1.** Abundance of  $C_4H_9^+$  ions as a function of time: (a) ions from  $2.5 \times 10^{-6}$  Torr isobutane and  $0.17 \times 10^{-6}$  Torr  $CH_3CO_2H$ ; (b) ions from  $2.5 \times 10^{-6}$  Torr  $n$ -butane and  $0.25 \times 10^{-6}$  Torr  $CH_3CO_2H$ .

experiments which elucidate the structures of butyl ions in the radiolysis of butyl halides and hexanes. These experiments were carried out at approximately atmospheric pressures, corresponding to collision intervals of  $10^{-10}$ – $10^{-9}$  s.

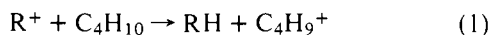
### Experimental Section

The experimental procedure for the ICR experiments was identical with that described in a previous study from this laboratory.<sup>6</sup> The temperature in the analyzer cell was kept at  $320 \pm 5$  K, and the electron energy was varied between  $10 \pm 1$  and  $25 \pm 2$  eV. Two- or three-component mixtures were prepared on a separate vacuum line. The premixed gases were stored in 550-mL spherical bulbs which could be attached to the manifold of the ICR.

The 300 K radiolysis experiments were also conducted according to procedures described in an earlier paper,<sup>5</sup> using the NBS  $^{60}Co$   $\gamma$  source. The intensity was  $2.5 \times 10^{-7}$  eV  $s^{-1}$  electron $^{-1}$ . Irradiation times varied between 3 and 15 h. Gas chromatographic analysis of products on a 12-m squalane column provided sufficient resolution to distinguish between deuterated and nondeuterated butanes produced in  $C_4H_9Br$ – $C_6D_{14}$  or  $C_6H_{14}$ – $C_6D_{14}$  mixtures. After quantitative analysis the butane products were analyzed by analytical mass spectrometry.

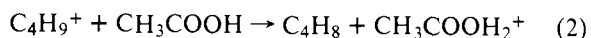
### Results and Discussion

**1. Hydride Ion Transfer from Butanes.** In  $n$ -butane and isobutane, the vast majority of the butyl ions are formed by well-known fast hydride transfer reactions:<sup>8</sup>



where  $R^+$  stands for the reactive hydrocarbon fragment ions such as  $C_2H_3^+$ ,  $C_2H_5^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ , etc.

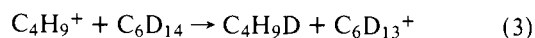
Tentatively accepting<sup>1–3,5,7</sup> that in a low-pressure gas-phase system the only  $C_4H_9^+$  ions which have to be considered are those with secondary or tertiary structures, the observation of differences in reactivity with selected molecules can be used to obtain quantitative information about the abundances of the two structures. This is illustrated in Figure 1, which shows an experimental tracing of the abundances of  $C_4H_9^+$  ions in butane and in isobutane, to which small quantities of  $CH_3COOH$  (proton affinity  $193.4 \pm 1$  kcal/mol)<sup>9,10</sup> have been added. The unreactive ions can be assigned the  $t$ - $C_4H_9^+$  structure, since for ions of this structure, the proton transfer reaction



is endothermic by about  $4 \pm 1$  kcal/mol.<sup>9,10</sup> On the other hand, accepting a value for  $\Delta H_f$  of  $sec$ - $C_4H_9^+$  of 175 kcal/mol,<sup>10</sup> reaction 2 would be  $8 \pm 2$  kcal/mol exothermic, and therefore the probable structure of the reactive  $C_4H_9^+$  is  $sec$ - $C_4H_9^+$ . The

value of  $k(2)$  for the reactive  $C_4H_9^+$  component formed in  $n$ -butane is  $10.5 \pm 1 \times 10^{-10}$  cm<sup>3</sup>/molecule·s. Similar results are obtained when  $(CH_3)_2O$  (proton affinity  $194 \pm 1$  kcal/mol)<sup>9,10</sup> is used as a proton acceptor.

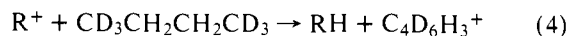
A different set of experiments was carried out with 3-methylpentane- $d_{14}$ , rather than acetic acid, as the reactant. As expected, the hydride ion transfer reaction



was observed. For  $C_4H_9^+$  ions originating from isobutane, which as indicated above have the tertiary structure,  $k(3)$  is small ( $0.15 \times 10^{-10}$  cm<sup>3</sup>/molecule·s). The  $C_4H_9^+$  ions generated in  $n$ -butane consist of a fast reacting ( $k(3) = 4.3 \pm 0.5 \times 10^{-10}$  cm<sup>3</sup>/molecule·s) and a slow reacting ( $k(3) = 0.2 \pm 0.1 \times 10^{-10}$  cm<sup>3</sup>/molecule·s) component, which can be ascribed to ions of the secondary and tertiary structures, respectively. Because in these experiments the additives are present in relatively small concentrations, the butyl ions should have no excess internal energy at the time of reaction. This is verified by the observation that the abundance ( $75 \pm 5\%$ ) and the rate constants measured for the reactive  $C_4H_9^+$  ions in  $n$ -butane are independent of the concentration of acetic acid (5–50%) or 3-methylpentane (10–50%).

The results presented here confirm the fact that  $sec$ - $C_4H_9^+$  ions can retain their structure for long periods of time in the absence of vibrational excitation. The activation energy for isomerization to the thermodynamically more stable  $t$ - $C_4H_9^+$  ion has been determined in the liquid phase to be  $\sim 17$ – $18$  kcal mol $^{-1}$ ,<sup>11</sup> and a similar energy barrier in the gas phase may be responsible for the observed stability of  $sec$ - $C_4H_9^+$ .

Experiments carried out using  $CD_3CH_2CH_2CD_3$  show that 80–90% of the  $C_4D_6H_3^+$  ions formed in the reaction



undergo a fast reaction with 3-methylpentane- $d_{14}$  ( $k = 4 \pm 1 \times 10^{-10}$  cm<sup>3</sup>/molecule·s). On the other hand, about 85% of the  $C_4D_5H_4^+$  ions, which are mainly formed by transfer of  $D^-$  from a primary position to the  $R^+$  species, were found to react very slowly with 3-methylpentane- $d_{14}$  ( $k \sim 0.2 \times 10^{-10}$  cm<sup>3</sup>/molecule·s). It follows that the majority of the  $sec$ -butyl ions formed in reaction 4 retain their structure, while the  $C_4D_5H_4^+$  ions, which initially possess the primary structure, would have sufficient energy to isomerize to the observed tertiary structure.

**2. Fragmentation of Alkane Ions.** In the case of the pentanes and hexanes, the butyl ions are exclusively formed by fragmentation of the parent ion. As expected, butyl ions formed in the fragmentation of neopentane, 2-methylpentane, and 2,2-dimethylbutane parent ions are unreactive toward the parent molecule as well as toward  $CH_3COOH$ , and can therefore be assigned the tertiary structure. In pure  $n$ -pentane and  $n$ -hexane, a fraction of the butyl ions undergo a rather fast hydride transfer reaction with the  $n$ -alkane ( $k = 2 \pm 1 \times 10^{-10}$  cm<sup>3</sup>/molecule·s), while the remaining butyl ions are entirely unreactive. Because of the endothermicity of the reaction of  $t$ - $C_4H_9^+$  with  $n$ -pentane and  $n$ -hexane, the unreactive  $C_4H_9^+$  component can be assigned the tertiary structure. The reactive  $sec$ - $C_4H_9^+$  ion constitutes  $25 \pm 2$  and  $34 \pm 2\%$  in  $n$ -pentane and  $n$ -hexane, respectively. Analogous experiments with 3-methylpentane- $h_{14}$  and  $-d_{14}$  show a similar abundance ( $25 \pm 3\%$ ) of  $sec$ - $C_4H_9^+$ . No discernible change in the relative abundance was noted over the electron energy range 12–25 eV.

In view of the fact that Semeluk and Lossing<sup>10</sup> have shown that the appearance potential of the  $C_4H_9^+$  originating from  $n$ - $C_5H_{12}$  corresponds to that which would be expected for ions of the secondary structure rather than the thermodynamically more stable  $t$ - $C_4H_9^+$  structure, it would seem that the rather high abundance of the  $t$ - $C_4H_9^+$  ions found in this study may

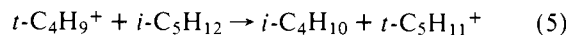
**Table I.** Butyl Ion Structures in *sec*-Butyl Bromide. Effect of Additive<sup>a</sup>

% CH <sub>3</sub> COOH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> <sup>+</sup> / <i>sec</i> -C <sub>4</sub> H <sub>9</sub> <sup>+</sup>
40	1.18
14	3.57
4	8.33
% 3-methylpentane	<i>t</i> -C <sub>4</sub> H <sub>9</sub> <sup>+</sup> / <i>sec</i> -C <sub>4</sub> H <sub>9</sub> <sup>+</sup>
50	1.28
9	3.57

<sup>a</sup> Pressure of *sec*-C<sub>4</sub>H<sub>9</sub>Br, 10<sup>-6</sup> Torr. Electron energy, 22 eV.

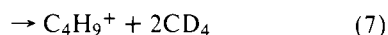
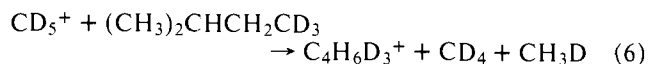
have to be accounted for by the isomerization of primary C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions formed in the initial cleavage of the C-C bond in the *n*-alkane, or by isomerization of internally excited *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions.

In the case of isopentane, *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions account for 37 ± 7% of the C<sub>4</sub>H<sub>9</sub><sup>+</sup> population at energies ranging from 13 to 28 eV. These ions react with isopentane with a rate constant of 3.2 ± 0.5 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-s. The remaining C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions exhibit a rate constant of 0.1 ± 0.05 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-s, in good agreement with the value of 0.16 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-s reported by Meot-Ner and Field<sup>13</sup> for the reaction



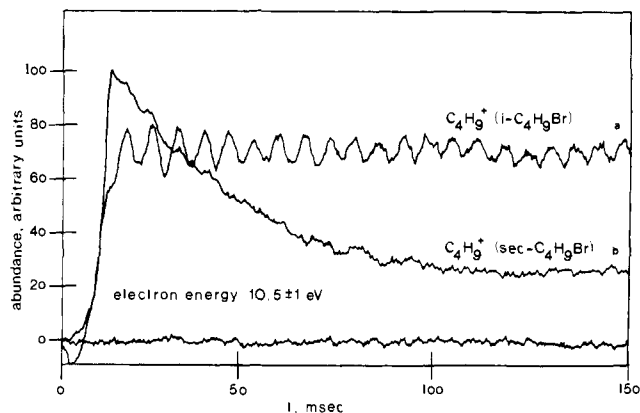
A better insight into the origin of the *sec*-butyl ions is obtained by examining the time dependence of the abundances of the C<sub>4</sub>H<sub>9</sub><sup>+</sup> and C<sub>4</sub>H<sub>6</sub>D<sub>3</sub><sup>+</sup> ions formed in the fragmentation of (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CD<sub>3</sub>. At a nominal electron energy of 20 eV, the C<sub>4</sub>H<sub>6</sub>D<sub>3</sub><sup>+</sup> ions, which correspond to approximately 85% of the butyl ions, show, within experimental error, the same fraction (~40%) of *sec*-butyl ions as observed for nonlabeled isopentane. Because of their low abundance, the composition of the C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions could not be established. Additional energy was imparted to (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CD<sub>3</sub> by use of xenon as a sensitizer. The lowest energy state of the Xe<sup>+</sup> ion is 12.12 eV,<sup>10</sup> ionization of isopentane requires 10.32 eV,<sup>10</sup> so electron transfer will form the isopentane ion with internal energy of 1.8 eV. The succeeding decomposition of the isopentane ion to CH<sub>3</sub> and *sec*-C<sub>4</sub>H<sub>6</sub>D<sub>3</sub><sup>+</sup> requires 0.1 eV,<sup>10</sup> so 1.7 eV remains in the fragments. If one assumes an equipartition of this energy, the *sec*-C<sub>4</sub>H<sub>6</sub>D<sub>3</sub><sup>+</sup> ion will be formed with internal energy of approximately 1.3 eV, or 30 kcal mol<sup>-1</sup>, an amount far in excess of that required for isomerization.<sup>11</sup> As expected, all of the C<sub>4</sub>H<sub>6</sub>D<sub>3</sub><sup>+</sup> ions formed in this experiment show the low reactivity towards isopentane characteristic of the *tert*-butyl ion.

Experiments were also performed in which excess CD<sub>4</sub> was added to (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CD<sub>3</sub>. In these experiments, the two dissociative proton transfer reactions



occur roughly in the ratio 2:1. Interestingly, while about 70% of the C<sub>4</sub>H<sub>6</sub>D<sub>3</sub><sup>+</sup> ions exhibit the *sec*-butyl reactivity, within experimental error, all C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions were found to show the same reactivity toward isopentane as the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions. Apparently, the isobutyl ions formed in reaction 7 rearrange to the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> structure.

**3. Fragmentation of the Butyl Halides.** When CH<sub>3</sub>COOH, (CH<sub>3</sub>)<sub>2</sub>O, or 3-methylpentane-*d*<sub>14</sub> is added to *i*-C<sub>4</sub>H<sub>9</sub>Br, *t*-C<sub>4</sub>H<sub>9</sub>Br, *sec*-C<sub>4</sub>H<sub>9</sub>Br, *n*-C<sub>4</sub>H<sub>9</sub>Br, and *sec*-C<sub>4</sub>H<sub>9</sub>Cl, the following observations are made: (1) The C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions from *i*-C<sub>4</sub>H<sub>9</sub>Br and *t*-C<sub>4</sub>H<sub>9</sub>Br are within experimental error entirely unreactive toward CH<sub>3</sub>COOH or (CH<sub>3</sub>)<sub>2</sub>O and react with

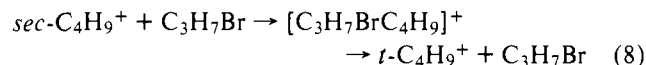


**Figure 2.** Abundance of C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions as a function of time: (a) ions from 6.9 × 10<sup>-7</sup> Torr isobutyl bromide and 7.0 × 10<sup>-7</sup> Torr (CH<sub>3</sub>)<sub>2</sub>O; (b) ions from 6.2 × 10<sup>-7</sup> Torr *sec*-butyl bromide and 6.5 × 10<sup>-7</sup> Torr (CH<sub>3</sub>)<sub>2</sub>O.

C<sub>6</sub>D<sub>14</sub> at the same rate as that observed for the C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions in *i*-C<sub>4</sub>H<sub>10</sub>-C<sub>6</sub>D<sub>14</sub> mixtures. (2) The C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions from *sec*-C<sub>4</sub>H<sub>9</sub>Br, *sec*-C<sub>4</sub>H<sub>9</sub>Cl, and *n*-C<sub>4</sub>H<sub>9</sub>Br, like those generated in *n*-butane, show a reactive and a less reactive or unreactive fraction. One of these reacts with CH<sub>3</sub>COOH, (CH<sub>3</sub>)<sub>2</sub>O, and 3-methylpentane with the same rates as those measured for the reactive component in *n*-butane. The other isomeric C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion is unreactive toward CH<sub>3</sub>COOH and (CH<sub>3</sub>)<sub>2</sub>O, and reacts slowly with 3-methylpentane (*k* = 0.2 ± 0.1 × 10<sup>-10</sup> cm<sup>3</sup>/molecule-s). Some of these results are shown in Figure 2.

It follows from these observations that ≥95% of the C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions from *i*-C<sub>4</sub>H<sub>9</sub>Br and *t*-C<sub>4</sub>H<sub>9</sub>Br have the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> structure, while those formed in the fragmentation of *sec*- and *n*-butyl halides consist of both *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> and *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions.

The relative abundance of the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions formed in the fragmentation of the linear alkyl halide parent ions depends on the concentration of acetic acid or 3-methylpentane (see Table I). Apparently, collisions with halide molecules can convert *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions into *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ions. This collision-induced isomerization process was confirmed by a series of experiments involving the addition of various concentrations of propyl bromide to a *n*-C<sub>4</sub>H<sub>10</sub>-CH<sub>3</sub>COOH (10:1) mixture, where it was found that, while in the absence of propyl bromide the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion was the most abundant isomeric species (80%), addition of increasing concentrations of propyl bromide eventually reduces the abundance of the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion species below its detection limit (less than 5% of the C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion yield). The collision-induced isomerization does not take place to any appreciable extent when, instead of propyl bromide, other unreactive molecules such as formaldehyde or formic acid are added to the C<sub>4</sub>H<sub>10</sub>-CH<sub>3</sub>COOH mixture. It seems plausible that the butyl ion isomerization occurs via a transient dialkylhalonium ion, e.g.



Although the intermediate could not be detected in the ICR, its lifetime must be fairly long since dialkylhalonium ions have been observed in mass spectrometric investigations.<sup>14</sup> The halide molecule apparently plays the role of a catalyst in overcoming the energy barrier associated with the isomerization. The efficiency of the halide-induced isomerization increases with increasing basicity of the halogen atom. For instance, while on the average one collision in five of the *sec*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion with *sec*-butyl bromide leads to isomerization to the *t*-C<sub>4</sub>H<sub>9</sub><sup>+</sup> ion structure, approximately five times that many collisions with *sec*-butyl chloride are needed to achieve the

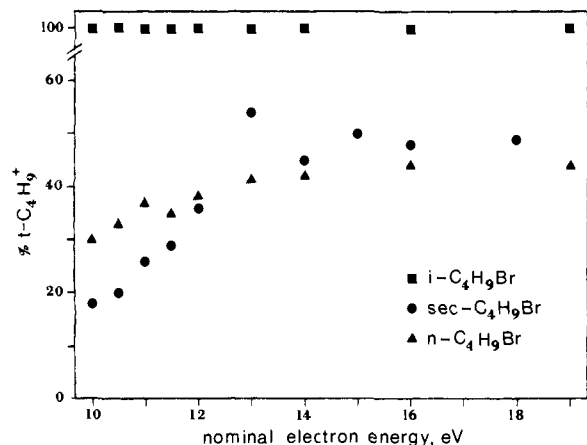
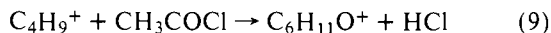


Figure 3. Percent  $t\text{-C}_4\text{H}_9^+$  ion as a function of electron energy, from  $i\text{-C}_4\text{H}_9\text{Br}$ ,  $n\text{-C}_4\text{H}_9\text{Br}$ , and  $sec\text{-C}_4\text{H}_9\text{Br}$ .

same result. In the absence of collision-induced isomerization, the limiting percentage of butyl ion possessing the  $sec\text{-C}_4\text{H}_9^+$  structure is  $57 \pm 4$ ,  $56 \pm 4$ , and  $48 \pm 4\%$ , for  $n\text{-C}_4\text{H}_9\text{Br}$ ,  $sec\text{-C}_4\text{H}_9\text{Br}$ , and  $sec\text{-C}_4\text{H}_9\text{Cl}$ , respectively, at electron energies ranging from 14 to 19 eV. As electron energy decreases further, to a nominal energy of  $10 \pm 1$  eV, which approximates the appearance potential of the secondary ion,<sup>10</sup> the amount of tertiary ion decreases (Figure 3) to approximate values of 17%  $t\text{-C}_4\text{H}_9^+$  for  $sec\text{-C}_4\text{H}_9\text{Br}$  and 30%  $t\text{-C}_4\text{H}_9^+$  for  $n\text{-C}_4\text{H}_9\text{Br}$ . At all energies the  $i\text{-C}_4\text{H}_9\text{Br}$  shows, within experimental error ( $\pm 5\%$ ), exclusively tertiary ion formation.

**4. Comparison with Collisional Activation.** In a recent collisional activation study<sup>3</sup> the conclusion was reached that isobutyl ions produced in the fragmentation of isobutyl bromide rearrange mainly to the  $sec\text{-C}_4\text{H}_9^+$  structure. This was based on a comparison of the fragmentation patterns of  $\text{C}_6\text{H}_{11}\text{O}^+$  ions formed in a reaction of butyl ions from isobutyl bromide and other precursor compounds, in the presence of added  $\text{CH}_3\text{COCl}$ . This reaction was suggested to be



In an attempt to explain the differences in the conclusions of that study and those reported here, we examined the reactivities of the butyl ions in the various systems with  $\text{CH}_3\text{COCl}$ . The butyl ions generated in isobutane,  $t\text{-C}_4\text{H}_9\text{Br}$ , and  $i\text{-C}_4\text{H}_9\text{Br}$  react very slowly with  $\text{CH}_3\text{COCl}$  ( $k < 10^{-11}$   $\text{cm}^3/\text{molecule}\cdot\text{s}$ ), while a fraction of the  $\text{C}_4\text{H}_9^+$  ions formed in  $sec\text{-}$  and  $n\text{-C}_4\text{H}_9\text{Br}$  undergo a fast reaction ( $k = 9 \pm 1 \times 10^{-10}$   $\text{cm}^3/\text{molecules}$ ) to form  $\text{CH}_3\text{CO}^+$  (Figure 4):



Such a reaction is exothermic by  $1.3 \pm 1$  kcal/mol when  $\text{C}_4\text{H}_9^+$  has the secondary structure, and is endothermic<sup>15</sup> for  $t\text{-C}_4\text{H}_9^+$  ions. The possibility that the  $\text{CH}_3\text{CO}^+$  product ion is formed in a dissociation of a  $\text{C}_6\text{H}_{11}\text{O}^+$  intermediate produced in reaction 9 can be ruled out; such a reaction sequence would be endothermic by more than 10 kcal/mol for both butyl ion structures.

The  $\text{C}_6\text{H}_{11}\text{O}^+$  ion which could be formed in reaction 9 was indeed observed in small abundance ( $< 5\%$  of the butyl ion abundance) in the mixtures of butyl halides with  $\text{CH}_3\text{COCl}$ , and double resonance ejection experiments confirmed that this product indeed results from a reaction of  $\text{C}_4\text{H}_9^+$  species. The kinetics of formation of  $\text{C}_6\text{H}_{11}\text{O}^+$  offers some clues about the origin of this product. (1) The rate of formation of  $\text{C}_6\text{H}_{11}\text{O}^+$  is essentially the same no matter which precursor of butyl ions is used. (2) The  $\text{C}_6\text{H}_{11}\text{O}^+$  ion abundance increases slowly as a function of time, and continues to increase at the same rate even after all the  $sec\text{-C}_4\text{H}_9^+$  ions have been removed by the

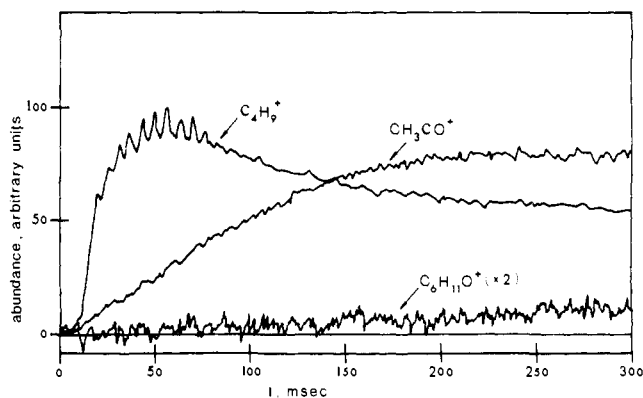


Figure 4. Abundance of ions in 2- $\text{C}_4\text{H}_9\text{Cl}$ - $\text{CH}_3\text{COCl}$  (10:1), total pressure  $1.8 \times 10^{-6}$  Torr.

occurrence of reaction 10 (see Figure 4). These two observations suggest that the major precursor of  $\text{C}_6\text{H}_{11}\text{O}^+$  may be the  $tert\text{-}$ butyl ion.

More important, the actual abundance of  $\text{C}_6\text{H}_{11}\text{O}^+$  observed in any particular mixture under given conditions is not reproducible, but depends directly on the length of time the  $\text{CH}_3\text{COCl}$ -containing mixture has been flowing through the ICR instrument. Apparently a surface reaction involving  $\text{CH}_3\text{COCl}$  results in the buildup of some compound which reacts with  $t\text{-C}_4\text{H}_9^+$  to give  $\text{C}_6\text{H}_{11}\text{O}^+$ . Acetic acid and/or acetic anhydride are possible identities of the unknown reactant compound, since (1) small abundances of ions of mass corresponding to protonated acetic acid and acetic anhydride were observed, and (2) the  $\text{C}_6\text{H}_{11}\text{O}^+$  ion is formed as a product in mixtures of isobutane with these compounds also. However, the possibility that other impurities may also react with  $t\text{-C}_4\text{H}_9^+$  to form  $\text{C}_6\text{H}_{11}\text{O}^+$  cannot be excluded.

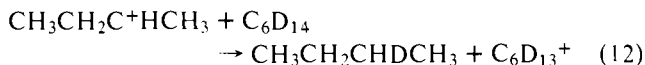
In summary, under our experimental conditions  $\text{C}_6\text{H}_{11}\text{O}^+$  is exclusively formed by reaction of  $t\text{-C}_4\text{H}_9^+$  with an as yet unidentified neutral molecule.

## 5. Radiolysis

In order to examine butyl ions which have existed for a much shorter time before undergoing reaction, butyl bromides and other butyl ion precursors were irradiated with  $^{60}\text{Co}$ - $\gamma$  rays at pressures from 15 to 100 Torr, in the presence of 0.4–5%  $\text{O}_2$  added as a free-radical scavenger. When nondeuterated butyl bromides are irradiated in the presence of 3-methylpentane- $d_{14}$ ,  $t\text{-C}_4\text{H}_9^+$  ions will react to give  $(\text{CH}_3)_3\text{CD}^5$



while  $sec\text{-C}_4\text{H}_9^+$  ions will react as follows:<sup>5</sup>



The relative yields of the neutral butane products,  $(\text{CH}_3)_3\text{CD}$  and  $\text{CH}_3\text{CH}_2\text{CHDCH}_3$ , reflect the relative abundances of  $t\text{-C}_4\text{H}_9^+$  and  $sec\text{-C}_4\text{H}_9^+$ , respectively.

When  $sec\text{-}$ butyl bromide was irradiated in the presence of a three- to fourfold excess of 3-methylpentane- $d_{14}$  (97 Torr total pressure),  $n\text{-}$ butane and isobutane were formed in a 99:1 ratio. Similar results are found when 2,3-dimethylbutane is used as the reactive interceptor. Thus within  $10^{-10}$ – $10^{-9}$  s there is no significant isomerization of  $sec\text{-C}_4\text{H}_9^+$  to  $t\text{-C}_4\text{H}_9^+$ . The vibrational deactivation caused by the collisions at high pressures apparently produces stable secondary ions which do not rearrange on this time scale. This observation is consistent with the results found in the ICR experiments when the electron energy was reduced (Figure 3).

When isobutyl bromide was similarly irradiated in the

presence of a 16.5-fold excess of 3-methylpentane- $d_{14}$  (82 Torr total pressure), product analysis showed an isobutane: $n$ -butane ratio of 12.6:1. Analysis of the butanes formed in this experiment shows that 37% consist of the expected  $(\text{CH}_3)_3\text{CD}$ , while 56% consist of  $i$ - $\text{C}_4\text{H}_{10}$ , derived presumably from a competing reaction of  $t$ - $\text{C}_4\text{H}_9^+$  with the  $\text{C}_4\text{H}_9\text{Br}$ . (The chemistry occurring in the radiolysis of alkyl halides is not as well understood as that involving alkanes).<sup>16</sup> The remaining 7% is  $\text{CH}_3\text{CHDCH}_2\text{CH}_3$ . Even neglecting the contribution of the  $i$ - $\text{C}_4\text{H}_{10}$ , this result indicates that a minimum of 85% of the butyl ions derived from isobutyl bromide acquire the tertiary structure within  $10^{-10}$  s after their formation.

Although a 1,2 hydride shift to form the  $t$ - $\text{C}_4\text{H}_9^+$  ion is the predominant mode of rearrangement of initially formed  $i$ - $\text{C}_4\text{H}_9^+$  ions, there seems to be a fraction of these ions which rearrange to the secondary structure, in accord with liquid-phase observations.<sup>4</sup> This rearrangement may proceed via a protonated methylcyclopropane intermediate.<sup>11</sup> Since the conversion from  $i$ - $\text{C}_4\text{H}_9^+$  to  $sec$ - $\text{C}_4\text{H}_9^+$  is exothermic by about 15 kcal/mol,<sup>17</sup> a certain fraction of the  $i$ - $\text{C}_4\text{H}_9^+$  ions appear to follow this permissible reaction course. The secondary ions so formed would initially have at least this 15 kcal/mol internal vibrational energy, which is comparable to the energy barrier of about 17 kcal/mol<sup>11</sup> for rearrangement to  $t$ - $\text{C}_4\text{H}_9^+$ . In high-pressure gases as well as in the liquid phase, this energy may be rapidly collisionally quenched, resulting in the appearance of measurable amounts of stable secondary ions. At the low pressures characteristic of the ICR experiments, however, any excited secondary ions will have had time to further rearrange to the most stable  $t$ - $\text{C}_4\text{H}_9^+$  structure before stabilizing collisions occur. As a result no secondary ions appear from  $i$ - $\text{C}_4\text{H}_9\text{Br}$  in the ICR experiments. The fraction of ions which follow this path is certainly small; initially formed 1- $\text{C}_4\text{H}_9^+$  ions (whose heat of formation is similar to that of  $i$ - $\text{C}_4\text{H}_9^+$ ) are predominantly stabilized in the 2- $\text{C}_4\text{H}_9^+$  structure under radiolysis conditions (Table II). Taking the yield of  $n$ -butane in the  $i$ - $\text{C}_4\text{H}_9\text{Br}$  experiment as an approximate measure of the maximum fraction of the isobutyl ions which undergo carbon skeleton rearrangement, one arrives at an estimate that  $90 \pm 5\%$  of the initially formed  $i$ - $\text{C}_4\text{H}_9^+$  ions undergo a 1,2-hydride shift.

To examine the structures of butyl ions formed in the radiolysis of alkanes, 1:1 mixtures of 3-methylpentane- $d_{14}$  and  $n$ -hexane were irradiated. The butyl ions can undergo reactions 11 and 12;  $sec$ -butyl ions can also abstract a hydride ion from the  $n$ -hexane. In these experiments, most of the butane formed has the normal structure, and the relative abundance of  $(\text{CH}_3)_3\text{CD}$  and  $(\text{CD}_3)_3\text{CD}$  decreases with increasing pressure (Table II). Apparently the isomerization of some of the linear butyl ions formed initially from these hexanes occurs in a time scale comparable to the collision interval ( $\sim 10^{-8}$ – $10^{-10}$  s). Butyl ions are formed in these radiolysis experiments with internal energies which enable unimolecular isomerization to occur despite the significant energy barrier. However, the collisions which the ions eventually will undergo effectively remove the extra energy so that most of the ions are frozen in the higher energy  $sec$ - $\text{C}_4\text{H}_9^+$  form.

## Conclusions

All butyl ions examined in this study formed from precursor molecules having an  $i$ - $\text{C}_4\text{H}_9$  or  $t$ - $\text{C}_4\text{H}_9$  group exist primarily as the  $t$ - $\text{C}_4\text{H}_9^+$  ion. This is true for ions observed either  $10^{-10}$  or  $10^{-2}$  s after formation (radiolysis and ICR experiments). That is, initially formed  $t$ - $\text{C}_4\text{H}_9^+$  ions do not rearrange, and

**Table II.** Extent of Isomerization of Butyl Ions from Fragmentation of Hexanes, as a Function of Pressure

parent molecule	pressure, Torr	collision interval, s	$tert$ -butyl/ $sec$ -butyl
$n$ -hexane	$10^{-6}$	$2 \times 10^{-2}$	1.92
	$\sim 1$	$\sim 2 \times 10^{-8}$	0.38 <sup>a</sup>
	11	$2 \times 10^{-9}$	0.22
3-methylpentane- $d_{14}$	116	$2 \times 10^{-10}$	0.125
	$10^{-6}$	$2 \times 10^{-2}$	3.12
	11	$2 \times 10^{-9}$	0.19
	116	$2 \times 10^{-10}$	0.071

<sup>a</sup> T. Y. Yu and F. H. Field, *Org. Mass Spectrom.*, **8**, 267 (1974).

$i$ - $\text{C}_4\text{H}_9^+$  ions rearrange almost entirely to the  $t$ - $\text{C}_4\text{H}_9^+$  structure within  $10^{-10}$  s. Butyl ions formed from precursors having a  $n$ - $\text{C}_4\text{H}_9$  or  $sec$ - $\text{C}_4\text{H}_9$  structure, however, are found to have both the secondary and tertiary structures. The fact that little secondary ion is formed from any isobutyl precursor indicates that the major pathway for isomerization of this structure need not involve significant formation of the secondary ion or the protonated methylcyclopropane species as suggested recently.<sup>3</sup> Instead, the bulk of the reaction may be adequately accounted for by the facile 1,2 hydrogen atom shift, to form  $t$ - $\text{C}_4\text{H}_9^+$ . The extent of isomerization from the  $sec$ - $\text{C}_4\text{H}_9^+$  structure to the more stable  $t$ - $\text{C}_4\text{H}_9^+$  structure depends on the fraction of the initially formed ions which have sufficient internal energy to overcome the energy barrier for isomerization, and on the time available for the rearrangement to occur. Isomerization is facilitated by collisions with halide molecules. The scope and mechanisms of collision-induced isomerizations will be discussed in a future publication.

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## References and Notes

- (1) M. S. B. Munson, *J. Am. Chem. Soc.*, **89**, 1772 (1967).
- (2) M. S. B. Munson, *J. Am. Chem. Soc.*, **90**, 83 (1968).
- (3) P. P. Dymerski and F. W. McLafferty, *J. Am. Chem. Soc.*, **98**, 6070 (1976).
- (4) G. J. Karabatsos, N. Hsi, and S. Meyerson, *J. Am. Chem. Soc.*, **92**, 621 (1970).
- (5) S. G. Lias, R. E. Rebert, and P. Ausloos, *J. Am. Chem. Soc.*, **92**, 6430 (1970).
- (6) Jo-Anne A. Jackson, S. G. Lias, and P. Ausloos, *J. Am. Chem. Soc.*, **99**, 7515 (1977).
- (7) J. R. Hass and K. R. Jennings, *Adv. Mass Spectrom.*, **6**, 711 (1974).
- (8) L. W. Sieck and S. G. Lias, *J. Phys. Chem. Ref. Data*, **5**, 1123 (1976).
- (9) (a) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. J. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977); (b) R. Yamdagni and P. Kebarle, *ibid.*, **98**, 1320 (1976).
- (10) Heats of formation of  $164 \pm 1$  and  $175 \pm 1$  kcal/mol are ascribed to the  $t$ - $\text{C}_4\text{H}_9^+$  and  $sec$ - $\text{C}_4\text{H}_9^+$  ions, respectively. A full discussion of the derivation of these and related values will be presented in a future publication. D. M. Shold, S. G. Lias, and P. Ausloos, unpublished results.
- (11) For a review see D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9**, 179 (1972).
- (12) P. Ausloos and S. G. Lias, *J. Am. Chem. Soc.*, **92**, 5037 (1970).
- (13) M. Meot-Ner and F. H. Field, *J. Chem. Phys.*, **64**, 277 (1976).
- (14) S. G. Lias, A. Viscomi, and F. H. Field, *J. Am. Chem. Soc.*, **96**, 359 (1974), and references cited therein.
- (15) Taking a value of  $154 \pm 1$  kcal/mol for  $\Delta H_f^\circ$  of  $\text{CH}_3\text{CO}^+$  (S. G. Lias and P. Ausloos in "Kinetics of Ion-Molecule Reactions", Plenum Press, New York, N.Y., 1978) the enthalpy of reaction 10 is  $-1.3 \pm 1$  and  $+4.7$  kcal/mol for  $sec$ - $\text{C}_4\text{H}_9^+$  and  $t$ - $\text{C}_4\text{H}_9^+$ , respectively.
- (16) S. G. Lias and P. Ausloos, "Ion-Molecule Reactions; Their Role in Radiation Chemistry", American Chemical Society, Washington, D.C., 1975.
- (17) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).