

Chemical Ionization Mass Spectra. XXI.

Reactions in $t\text{-C}_5\text{H}_{11}\text{Cl}$, $t\text{-C}_5\text{H}_{11}\text{Br}$, $t\text{-C}_5\text{H}_{11}\text{OH}$, and $t\text{-C}_5\text{H}_{11}\text{SH}$ S. G. Lias,¹ A. Viscomi, and F. H. Field**Contribution from The Rockefeller University,
New York, New York 10021. Received June 16, 1973*

Abstract: Mixtures of isobutane with small amounts (0.01–1%) of added $t\text{-C}_5\text{H}_{11}\text{Cl}$, $t\text{-C}_5\text{H}_{11}\text{Br}$, $t\text{-C}_5\text{H}_{11}\text{OH}$, and $t\text{-C}_5\text{H}_{11}\text{SH}$ have been studied in a high-pressure mass spectrometer as a function of total pressure, temperature, and concentration of additive. It is seen that proton transfer occurs only to $t\text{-C}_5\text{H}_{11}\text{SH}$, and even in this case, proton transfer is a minor process. The major reaction observed with each of the four molecules is the formation of a condensation ion which dissociates rapidly to give $(\text{C}_9\text{H}_{19}^+ + \text{HX})$ or $(\text{C}_6\text{H}_{11}^+ + \text{neutral products})$ where X is Cl, Br, OH, or SH. The formation of $\text{C}_6\text{H}_{11}^+$ is favored under all conditions, but the formation of $\text{C}_9\text{H}_{19}^+$ becomes more important as the pressure is raised or the temperature is lowered. When $i\text{-C}_4\text{D}_{10}$ is substituted for $t\text{-C}_4\text{H}_{10}$, it is seen that in the mercaptan, where proton transfer may be slightly exothermic, the departing hydrogen sulfide molecule carries away a D species from the reacting *tert*-butyl ion with a high probability; conversely, in $t\text{-C}_5\text{H}_{11}\text{Br}$, the departing hydrogen bromide molecule has a low probability of containing a hydrogen species from the reacting *tert*-butyl ion. This result suggests that when proton transfer competes with the displacement reaction, the two reactions proceed through the same intermediate ion, a $\text{C}_9\text{H}_{20}\text{X}^+$ species, in which "internal" proton transfer has occurred. The product $\text{C}_6\text{H}_{11}^+$ ion undergoes an analogous displacement reaction with all of these molecules to form the following as products: $(\text{C}_{10}\text{H}_{21}^+ + \text{HX})$ and $(\text{C}_6\text{H}_{13}^+ + \text{neutral products})$. The $\text{C}_6\text{H}_{13}^+$ product ion also undergoes a displacement reaction with all of these molecules to form as products $(\text{C}_{11}\text{H}_{23}^+ + \text{HX})$.

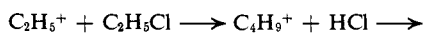
When a polar molecule containing a heteroatom (such as a halide, for example) interacts with a positive ion, it is often observed that one of the competing channels of reaction is a process which may be called a "displacement reaction." This is a process in which the initial interaction between the ion and molecule results in the formation of a condensation ion which has a very short lifetime with respect to a dissociation in which a stable neutral molecule containing the heteroatom is "displaced" from the condensation ion. For example, when the C_2H_5^+ ion reacts with vinyl chloride^{2–4} in a mass spectrometer at low pressures, a fraction of the ions react as follows.



The C_4H_5^+ product ion undergoes a similar reaction with vinyl chloride.



Analogous reactions have been observed in vinyl fluoride.⁵ Similarly, in a tandem mass spectrometric investigation⁶ of the reactions of various ions with ethyl chloride, it was seen that a fraction of the C_2H_4^+ ions and C_2H_5^+ ions reacted to displace a neutral HCl molecule.



Analogous displacements of hydrogen halides were observed in a study⁷ of the ion–molecule reactions

(1) Visiting Assistant Professor, 1971–1972, National Bureau of Standards Training Act.

(2) B. M. Hughes, T. O. Tiernan, and J. H. Futrell, *J. Phys. Chem.*, **73**, 829 (1969).

(3) J. A. Herman, J. J. Myher, and A. G. Harrison, *Can. J. Chem.*, **47**, 647 (1969).

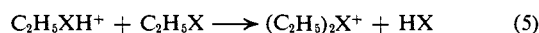
(4) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

(5) J. A. Herman and A. G. Harrison, *Can. J. Chem.*, **47**, 957 (1969).

(6) T. O. Tiernan and B. M. Hughes, *Advan. Chem. Ser.*, **82**, 412 (1968).

(7) J. L. Beauchamp, D. Holty, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972).

occurring in the methyl and ethyl halides. It was noted, for instance, that the protonated parent ions react with their respective parent molecules to displace a hydrogen halide molecule. For example, in the ethyl halides, the reaction



(where X is F, Cl, Br, or I) occurs. In the same study the reaction analogous to reaction 4 was observed in ethyl fluoride.



This paper reports a study of the ion–molecule reactions of the *tert*-butyl ion, and other ions generated in isobutane, with several molecules which are similar in structure (each contains a C_5H_{11} group) but which contain different heteroatoms or functional groups, namely $t\text{-C}_5\text{H}_{11}\text{Cl}$, $t\text{-C}_5\text{H}_{11}\text{Br}$, $t\text{-C}_5\text{H}_{11}\text{OH}$, and $t\text{-C}_5\text{H}_{11}\text{SH}$. As will be shown below, proton transfer from the *tert*-butyl ion to each of these molecules is either endothermic or close to thermoneutral. It will be shown that under these conditions, the occurrence of a displacement reaction involving loss of HX is a general phenomenon.

Experimental Section

The experiments were performed in the Rockefeller chemical physics mass spectrometer, equipped with the ion source designated as source III.⁸ The apparatus and technique have been described in previous papers.^{8,9} The repeller and focus electrodes were maintained at minimum operating potentials (5 V repeller and 6 V focus) needed to achieve a useable sensitivity.

Gas phase mixtures of $t\text{-C}_5\text{H}_{11}\text{Cl}$, $t\text{-C}_5\text{H}_{11}\text{Br}$, $t\text{-C}_5\text{H}_{11}\text{OH}$, and $t\text{-C}_5\text{H}_{11}\text{SH}$ in isobutane at known concentrations (1–10%) were prepared and kept in storage volumes. Isobutane gas at a known pressure was continuously flowed through the reaction chamber of the instrument; at the beginning of an experiment the mixture of interest was allowed to diffuse into the reaction

(8) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1567 (1971).

(9) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

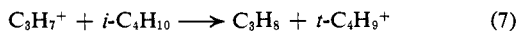
chamber through a gold foil leak. The increase in pressure in the reaction chamber was carefully measured, and the concentration of additive in the reaction chamber was calculated assuming that the composition of the mixture was not significantly changed in passing through the leak. Five to ten replicate determinations of the various spectra were made. The system was flushed with pure isobutane before and after every experimental point was taken.

Materials. The *t*-C₅H₁₁SH was technical grade obtained from Matheson Coleman and Bell (85% purity). It was purified by preparative scale gc to 99.5+ % purity. The *t*-C₅H₁₁Br and *t*-C₅H₁₁Cl were obtained from Chemical Samples Co., and the purities stated by the manufacturer were 92.4 and 98%, respectively. Efforts were made to purify the bromide by preparative scale gc and by distillation but without success. Thus, the materials were used as received, but no ions which could be identified as coming from impurities were found in the mass spectra. The *t*-C₅H₁₁OH was obtained from Matheson Coleman and Bell, and its purity was stated by the manufacturer as 99%. We detected no impurities by gc analyses, and the material was used as received.

The perdeuterated isobutane was obtained from Merck Sharp and Dohme of Canada and was purified chromatographically.

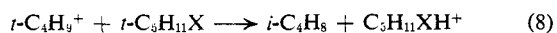
Results and Discussion

A number of studies from this laboratory¹⁰ have reported on the ion spectra (chemical ionization spectra) occurring in mixtures of isobutane with small amounts of other compounds added. In these experiments, isobutane reactant gas is introduced into the reaction chamber of the mass spectrometer at a total pressure of 0.2 to 3 Torr, and small amounts (0.01 to 1% of the total mixture) of the compound of interest are added. At these pressures, most of the fragment carbonium ions formed in the isobutane will react with the isobutane itself to form *tert*-butyl ions, *e.g.*



Thus, about 85–88% of the ions observed in pure isobutane at these pressures will be *t*-C₄H₉⁺ ions. Since the *tert*-butyl ion is unreactive with isobutane itself, it will survive to undergo collisions with the additive compound. In many cases, the *tert*-butyl ion has been seen to function as a weak Brønsted acid *vis-à-vis* the added compounds, so that the protonated parent ions of the additive molecule (or dissociation products of that ion) are often important in isobutane chemical ionization spectra.

Proton Affinities of *t*-C₅H₁₁Cl, *t*-C₅H₁₁Br, *t*-C₅H₁₁OH, and *t*-C₅H₁₁SH. This paper reports the observation of certain ion-molecule reaction sequences initiated by the reactions of the *tert*-butyl ion with added *t*-C₅H₁₁Cl, *t*-C₅H₁₁Br, *t*-C₅H₁₁OH, and *t*-C₅H₁₁SH. Before discussion of our observations, it is useful first to consider whether or not one would expect the proton transfer reactions



to be important in these experiments. The proton affinities of these four compounds are not known, but it is possible to make an estimate of their values by examining the trends in the proton affinities of the lower members of the several homologous series^{7,11,12} and assigning a value to the *t*-C₅H₁₁X compound on the basis of an educated guess; such estimates are given in the second column of Table I. Another method of estimating these proton affinities is to assume that the hydrogen affinities of the C₆H₁₁X⁺ ions are the same

(10) F. H. Field in "Ion-Molecule Reactions," J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, Chapter 6.

(11) J. Long and B. Munson, *J. Amer. Chem. Soc.*, **95**, 2427 (1973).

(12) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

Table I. Estimated Proton Affinities

Compd	Estimated proton affinity, kcal/mol	
	From PA's of lower members of homologous series ^a	From hydrogen affinities ^a
<i>t</i> -C ₅ H ₁₁ Cl	175	176
<i>t</i> -C ₅ H ₁₁ Br	178	178
<i>t</i> -C ₅ H ₁₁ OH	185–197	
<i>t</i> -C ₅ H ₁₁ SH	190–200	196
	Known proton affinity ¹¹	
<i>i</i> -C ₄ H ₈		195
CH ₃ CH=CH ₂		182

^a See discussion.

as those for the lower members of the respective homologous series (a good approximation since hydrogen affinities have been shown to be very similar for different members of a homologous series¹²). Then the proton affinities can be calculated from the relation

$$PA(RX) = IP(H) - IP(RX) - HA(RX^+)$$

(where PA(RX) is the proton affinity of the particular compound, IP refers to the ionization potentials of the designated species, and HA(RX⁺) is the hydrogen affinity of the corresponding parent ion). The hydrogen affinities of alkyl chlorides, bromides, alcohols, and mercaptans are respectively 107, 93, 117, and 91 kcal/mol.¹² Unfortunately, the ionization potentials of *t*-C₅H₁₁Cl, *t*-C₅H₁₁Br, *t*-C₅H₁₁OH, and *t*-C₅H₁₁SH are not known; in the case of the chloride, bromide, and mercaptan, the ionization potentials of the *t*-C₄H₉X compounds are, however, known,¹³ and these values have been used in estimating the proton affinities given in the last column of Table I. The proton affinities estimated in the two ways are in good agreement. Even though these are only estimated values of the proton affinities, it is clear from a comparison with the proton affinity of *i*-C₄H₈ (Table I) that proton transfer from a *t*-C₄H₉⁺ ion to *t*-C₅H₁₁Cl or *t*-C₅H₁₁Br is definitely endothermic and will not occur in our system at ordinary temperatures. The estimated proton affinity values for *t*-C₅H₁₁OH and *t*-C₅H₁₁SH are such that we cannot predict with certainty whether or not proton transfer from a *tert*-butyl ion would occur; such proton transfer reactions are definitely, however, not highly exothermic.

General Observations. Table II shows the relative intensities of the ions formed in the additive compounds as a result of interactions with the ions in isobutane in mixtures containing not more than 0.02% additive compound in isobutane, at a total pressure of 0.7 Torr and at 350°K. In view of our conclusion that proton transfer reaction 8 is not energetically favorable for the chloride and bromide, and only possibly favorable for the alcohol and mercaptan, it is not surprising that at this low concentration of additive ions corresponding to protonated compounds are not observed with intensities greater than the 2% lower limit applied in Table II. It is very striking that under these conditions, the identities of the major ions formed in reactions of *tert*-butyl ions with *t*-C₅H₁₁Cl, *t*-C₅H₁₁Br, *t*-C₅H₁₁OH, and *t*-C₅H₁₁SH are identical, and even the relative

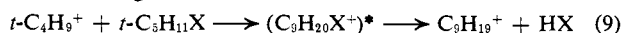
(13) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data. Ser., Nat. Bur. Stand.*, No. 26 (1969).

Table II. Chemical Ionization Mass Spectra^a of *t*-C₃H₁₁Cl, *t*-C₃H₁₁Br, *t*-C₃H₁₁OH, and *t*-C₃H₁₁SH with Isobutane Reactant Gas

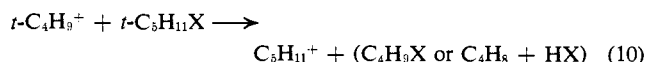
<i>m/e</i>	Ion	Relative abundances			
		<i>t</i> -C ₃ H ₁₁ Cl	<i>t</i> -C ₃ H ₁₁ Br	<i>t</i> -C ₃ H ₁₁ OH	<i>t</i> -C ₃ H ₁₁ SH
70	C ₃ H ₁₀ ⁺	10.6	7.7	5.3	6.7
71	C ₃ H ₁₁ ⁺	72.0	71.8	65.0	72.3
109	C ₈ H ₁₃ ⁺	3.3	3.3	3.3	3.2
127	C ₉ H ₁₉ ⁺	11.2	13.9	18.3	13.4

^a Ions generated in the additive have been normalized to 100%. Concentration of added compound in source <0.02%. In case of *t*-C₃H₁₁SH, concentration <0.005%. Total pressure, 0.7 Torr. Temperature, 350°K. (Ions comprising less than 2% of ionization in added compound have been omitted; corrections have been made for ¹³C isotopic abundance.)

abundances of the ions are similar. Since no ions containing heteroatoms are observed, we must conclude that these four compounds undergo analogous ion-molecule reactions with the *tert*-butyl ion resulting in the formation of neutral product containing the heteroatoms. In every case, the most important product ions are C₅H₁₁⁺ and C₉H₁₉⁺. The C₉H₁₉⁺ must be formed in a displacement reaction analogous to reactions 1 through 6 observed earlier



(where X is Cl, Br, OH, or SH). The C₃H₁₁⁺ may be formed through a simple X⁻ transfer reaction involving a "loose" reaction complex, through dissociation of a C₉H₂₀X⁺ condensation ion, or through dissociation of the C₉H₁₉⁺ ion produced in reaction 9. It is impossible from these results to distinguish between these processes, so we write



It should be pointed out that when the neutral product of reaction 10 is C₄H₉X, the reaction is formally an X⁻ transfer reaction and is probably endothermic for all these systems.

Further information about these systems is obtained from experiments at different concentrations of the additive compounds in the reaction chamber of the mass spectrometer. Table III shows the relative abundances of the ions formed in *t*-C₃H₁₁Cl, *t*-C₃H₁₁Br, *t*-C₃H₁₁OH, and *t*-C₃H₁₁SH as a result of interactions with ions from isobutane when the concentration of the additive is rather higher, *i.e.*, 0.3 to 0.5%. The behavior of *t*-C₃H₁₁Cl, *t*-C₃H₁₁OH, and *t*-C₃H₁₁Br is essentially the same under these conditions, but *t*-C₃H₁₁SH exhibits a greater tendency to produce stable condensation ions such as C₅H₁₁SHC₄H₉⁺ (*m/e* 161), C₅H₁₁SHC₃H₁₁⁺ (*m/e* 175), and the like. The spectra are complicated, but most features can readily be understood in terms of reactions 9 and 10 and their analogs.

Proton Transfer Reactions. Only in *t*-C₃H₁₁SH does the protonated parent ion occur (Table III), and this is compatible with our considerations of proton affinities given earlier. However, the variation of the intensity of C₅H₁₁SH₂⁺ is peculiar and indicates the possibility that the ion may not be formed in a straightforward way. In particular, the intensity is trivially small unless the concentration of *t*-C₃H₁₁SH is relatively high. Under the low-concentration conditions (*t*-C₃H₁₁SH ≤ 0.005%) of the experiment reported in Table II, the abundance of C₅H₁₁SH₂⁺ was only 0.42%, but

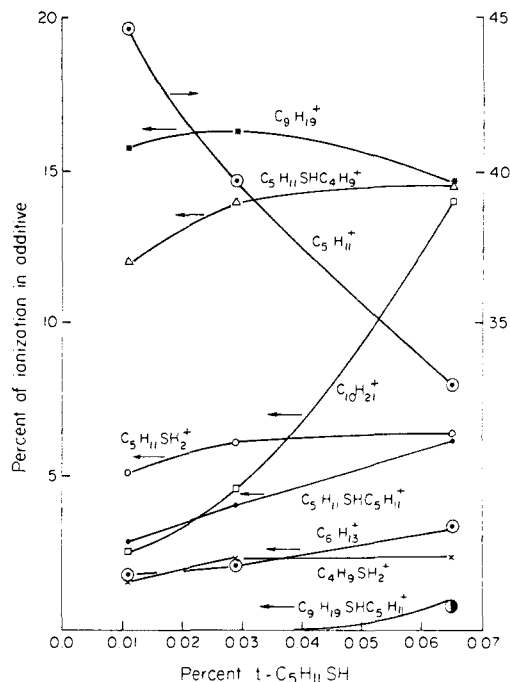


Figure 1. The relative intensities of selected product ions formed in various isobutane-*t*-C₃H₁₁SH mixtures at a total pressure of 0.8 Torr and 330°K.

Table III. Chemical Ionization Mass Spectra^a of *t*-C₃H₁₁Cl, *t*-C₃H₁₁Br, *t*-C₃H₁₁OH, and *t*-C₃H₁₁SH in Isobutane Reactant Gas under Conditions of High Concentration of Additive (0.3–0.5%) in Reaction Chamber of Mass Spectrometer

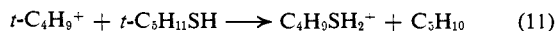
<i>m/e</i>	Ion	<i>t</i> -C ₃ H ₁₁ Cl	<i>t</i> -C ₃ H ₁₁ Br	<i>t</i> -C ₃ H ₁₁ OH	<i>t</i> -C ₃ H ₁₁ SH
70	C ₃ H ₁₀ ⁺	7.7	5.3	5.2	3.2
71	C ₃ H ₁₁ ⁺	58.5	45.4	62.9	13.9
83	C ₆ H ₁₁ ⁺	0.9	1.3	1.5	0.4
85	C ₆ H ₁₃ ⁺	5.7	10.5	1.4	2.3
91	C ₄ H ₉ SH ₂ ⁺				0.4
99	C ₇ H ₁₅ ⁺		0.2	0.7	0.3
105	C ₅ H ₁₁ SH ₂ ⁺				2.1
109	C ₈ H ₁₃ ⁺	2.4	2.1	3.2	1.5
113	C ₈ H ₁₇ ⁺	1.0	2.4	0.4	1.5
125	C ₉ H ₁₇ ⁺	0.5	0.1	0.1	
127	C ₉ H ₁₉ ⁺	10.8	9.6	17.7	8.6
139	C ₁₀ H ₁₉ ⁺	0.8	2.0	1.3	
141	C ₁₀ H ₂₁ ⁺	5.6	6.3	1.1	7.7
143	C ₅ H ₁₁ SHC ₃ H ₃ ⁺				1.0
145	C ₅ H ₁₁ OHC ₄ H ₉ ⁺			1.2	
147	C ₅ H ₁₁ SHC ₃ H ₇ ⁺				0.6
153	C ₁₁ H ₂₁ ⁺	0.5	1.8	0.6	
155	C ₁₁ H ₂₃ ⁺	1.1	2.9	1.1	0.7
161	C ₅ H ₁₁ SHC ₄ H ₉ ⁺				12.3
163	C ₅ H ₁₁ ClC ₄ H ₉ ^{+b}	0.1			
165		0.03			
175	C ₅ H ₁₁ SHC ₃ H ₁₁ ⁺				31.4
189	C ₅ H ₁₁ SHC ₆ H ₁₃ ⁺				3.0
193	C ₅ H ₁₁ BrC ₃ H ₇ ^{+b}		0.27		
195			0.26		
207	C ₅ H ₁₁ BrC ₄ H ₉ ^{+b}		0.24		
209			0.23		
221	C ₅ H ₁₁ BrC ₅ H ₁₁ ^{+b}		0.18		
223			0.16		
231	C ₅ H ₁₁ SHC ₅ H ₁₉ ⁺				2.3
245	C ₅ H ₁₁ SHC ₁₀ H ₂₁ ⁺				1.6

^a Total pressure, 0.7 Torr. Temperature, 350°K. ^b The natural abundances of ⁷⁹Br and ⁸¹Br are 50.5 and 49.5%, respectively. Those of ³⁵Cl and ³⁷Cl are 75.4 and 24.6%, respectively.

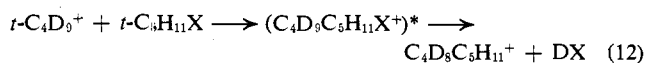
at higher concentrations of *t*-C₃H₁₁SH (0.01–0.07% in Figure 1 and 0.03–0.05% in Table III) the abundance

of $C_5H_{11}SH_2^+$ rose to 2–5%. On the other hand, no significant variation of $C_5H_{11}SH_2^+$ abundance with concentration is found in the results depicted in Figure 1. We offer no explanation for the details of this behavior.

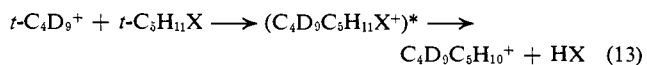
The $C_4H_9SH_2^+$ ion is also observed in $t-C_5H_{11}SH$ with small intensity (Table III), and this indicates the occurrence of a kind of alkyl exchange reaction.



The Displacement Reaction $C_4H_9^+ + t-C_5H_{11}X \rightarrow C_9H_{19}^+ + HX$. Information about the mechanism of the displacement reaction 9 can be obtained in experiments in which $i-C_4D_{10}$ is substituted for $i-C_4H_{10}$ as the reaction gas. In such an experiment, where the reactant ion is $t-C_4D_9^+$, it is possible to ascertain whether the departing molecule contains a hydrogen species from the reactant ion



or from the molecule



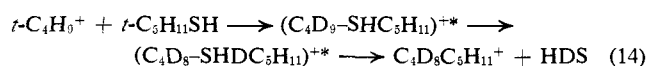
(It should be noted that the mass of $C_4D_9C_5H_{10}^+$ is the same as that of $(C_4D_{10})_2^+$ ion; however, the contribution of the isobutane dimer ion is minor compared to that of $C_4D_9C_5H_{10}^+$ under the conditions of these experiments.) The ratios of the two displacement reaction product ions, $C_4D_9C_5H_{10}^+/C_4D_8C_5H_{11}^+$, measured in these experiments are given in Table IV. Interestingly,

Table IV. Relative Amounts of Partially Deuterated Analog Ions Formed in $i-C_4D_{10}-t-C_5H_{11}X$ Mixtures^a

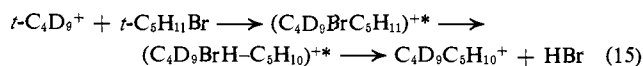
	$t-C_5H_{11}Br$	$t-C_5H_{11}OH$	$t-C_5H_{11}SH$
$C_4D_9C_5H_{10}^+-C_4D_8C_5H_{11}^+$	82:18	43:57	20:80
$C_5H_{10}D^+-C_5H_{11}^+$	46:54	4:96	23:77
$C_{10}H_{20}D^+-C_{10}H_{21}^+$	43:57	0:100	c
$C_6H_{12}D^+-C_6H_{13}^+$	44:56	0:100	40:60
$C_5D_7C_5H_{10}^+-C_5D_6C_5H_{11}^+$ ^b	54:46		

^a Total pressure, 0.7 Torr. Temperature, 350°K. ^b Observed only at concentrations of $t-C_5H_{11}Br$ greater than ~0.3%. ^c Not determined.

the relative importance of reactions 12 and 13 varies widely from one compound to another. In the alcohol, the hydrogen species in the product HX molecule comes from the ion or the molecule with approximately equal probability, while in the bromide, this hydrogen species comes predominantly from the $C_5H_{11}Br$ molecule. In the mercaptan, on the other hand, the departing molecule contains a hydrogen species which comes mainly from the reactant ion. These results can be explained if we take into account the fact that in the mercaptan, proton transfer from the ion to the molecule is more exothermic; the fact that most of the departing hydrogen sulfide species carry away a deuterium atom from the reactant ion suggests that in the intermediate for this a deuteron from the reacting ion has a high probability of being "transferred" to the SH group. These processes are represented for didactic purposes (no direct evidence about the structures exists) in reaction 14. On the other hand, in the bromide,

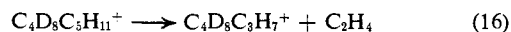


proton transfer is definitely endothermic, and it is unlikely that a D^+ species from a reacting ion will "transfer" to the $C_5H_{11}Br$ species in the ion-molecule complex. Rather, the species transferring are predominantly $H\cdot$ from $C_5H_{11}SH$. This is represented for didactic purposes in reaction 15. The alcohol



constitutes an intermediate case, in which the "internal proton transfer" in the intermediate occurs about 50% of the time. This behavior trend from mercaptan to alcohol to bromide is in keeping with our estimates of the proton affinities of the compounds.

The results listed in Table III show that a minor ion appears at mass 99, $C_7H_{15}^+$. Deuterium labeling experiments indicate that this ion originates from the dissociation of the $C_9H_{19}^+$ ion. That is, in the experiments with $t-C_4D_9^+$ as reactant ion, the only ions corresponding to $C_7H_{15}^+$ which were seen were $C_4D_8C_3H_7^+$ and $C_4D_9C_3H_6^+$, which can best be attributed to the reactions



Apparently, this dissociation involves mainly the loss of undeuterated C_2H_4 , suggesting that extensive rearrangement does not occur in the C_9 ion prior to this dissociation.

The Formation of $C_5H_{11}^+$. Reactions Initiated by $C_5H_{11}^+$. As discussed above, the $C_5H_{11}^+$ ion may be formed through a "direct" X^- transfer, through the dissociation of the *tert*-butyl ion- $C_5H_{11}X$ condensation ion, or through the dissociation of the $C_9H_{19}^+$ ion formed in reaction 9. Some information about the mode of formation of $C_5H_{11}^+$ can be obtained from the experiments in which $i-C_4D_{10}$ was substituted for $i-C_4H_{10}$ as reactant gas. In such experiments, both $C_5H_{11}^+$ and $C_5H_{10}D^+$ were formed. The relative abundances of these two analog ions formed in $t-C_5H_{11}Br$, $t-C_5H_{11}OH$, and $t-C_5H_{11}SH$ are given in Table IV. If the $C_5H_{11}^+$ ($C_5H_{10}D^+$) ion were formed primarily through dissociation of the C_9H_{19} analogs, it might be expected that when $(C_4D_9C_5H_{10})^+$ analogs predominate, as in $t-C_5H_{11}Br$ (Table IV), the dissociation would yield mainly $C_5H_{10}D^+$. No close correlation exists for $t-C_5H_{11}Br$ and $t-C_5H_{11}OH$, and we conclude that the formation of $C_5H_{11}^+$ from $C_9H_{19}^+$ is unlikely for these compounds. On the other hand, the results given in Table IV would allow the formation of $C_5H_{11}^+$ from $C_9H_{19}^+$ for $t-C_5H_{11}SH$, but of course they do not require it. No conclusion can be drawn for this compound. Turning now to the possibility of a direct X^- transfer reaction, we point out that these reactions are endothermic by several kilocalories per mole. Thus, they may be expected to have very low rate constants. Furthermore, the formation of $C_5H_{10}D^+$ ions rules out the occurrence of X^- transfer through a loose reaction complex. We are of the opinion that taken all together the evidence indicates that $C_5H_{11}^+$ ions are most probably formed by the dissociation of the $C_9H_{20}X^+$ condensation.

We investigated the effect of temperature on the spectra of $t-C_5H_{11}Br$, and the results obtained provide information about the reactions producing $C_5H_{11}^+$ and $C_9H_{19}^+$. Figure 2 shows two abundance ratios in

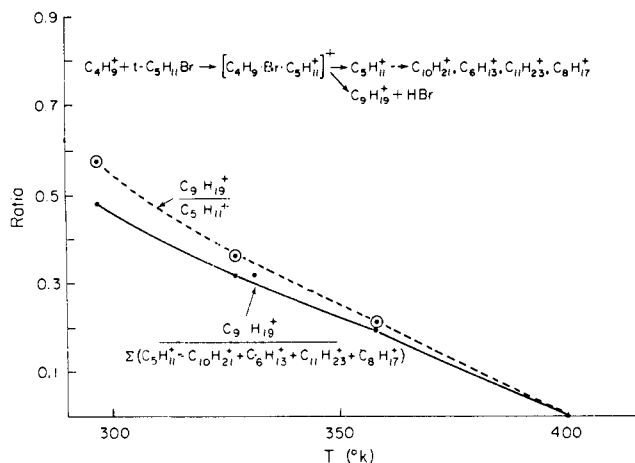
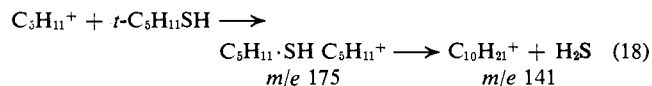


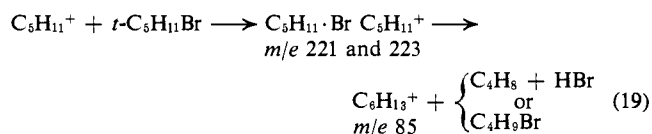
Figure 2. The effect of temperature on the reaction sequence: $t\text{-C}_4\text{H}_9^+ + t\text{-C}_5\text{H}_{11}\text{Br} \rightarrow \text{C}_9\text{H}_{19}^+$ and $\text{C}_5\text{H}_{11}^+$ ($+\text{C}_{10}\text{H}_{21}^+$, $\text{C}_6\text{H}_{13}^+$, $\text{C}_{11}\text{H}_{23}^+$, $\text{C}_8\text{H}_{17}^+$) observed in an $i\text{-C}_4\text{H}_{10}\text{-}t\text{-C}_5\text{H}_{11}\text{Br}$ (1:0.0003) mixture at pressures of 1.23 Torr.

$t\text{-C}_5\text{H}_{11}\text{Br}$ at several source temperatures. One ratio is the abundance of $\text{C}_9\text{H}_{19}^+$ ion to that of $\text{C}_5\text{H}_{11}^+$ ion, and the other ratio is the abundance of $\text{C}_9\text{H}_{19}^+$ ion to the sum of the abundances of $\text{C}_5\text{H}_{11}^+$ ion and the product ions formed from $\text{C}_5\text{H}_{11}^+$ ion, as discussed later. From Figure 2 it is seen that the importance of $\text{C}_9\text{H}_{19}^+$ formation diminishes drastically as the temperature increases. At pressures of about 1 Torr (the approximate pressure of the experiment), one would not expect to observe $\text{C}_9\text{H}_{19}^+$ ions at temperatures above about 400°K. Figure 3 shows that increasing the source pressure decreases the abundance of $\text{C}_5\text{H}_{11}^+$ and increases the abundance of $\text{C}_9\text{H}_{19}^+$. Both the temperature and pressure effects indicate that relatively highly excited $\text{C}_5\text{H}_{20}\text{X}^+$ intermediates dissociate to produce $\text{C}_3\text{H}_{11}^+$ ions, but less excited intermediates produce $\text{C}_9\text{H}_{19}^+$ ions (reaction 9).

The results given in Table III show that at high concentration of additive higher mass association ions ($\text{C}_5\text{H}_{11}\text{SHC}_9\text{H}_{19}^+$, $\text{C}_5\text{H}_{11}\text{BrC}_5\text{H}_{11}^+$, etc.) and various alkyl ions ($\text{C}_{11}\text{H}_{23}^+$, $\text{C}_{10}\text{H}_{21}^+$, $\text{C}_6\text{H}_{13}^+$, etc.) are produced in $t\text{-C}_5\text{H}_{11}\text{SH}$ and $t\text{-C}_5\text{H}_{11}\text{Br}$. The variations of intensities with additive concentrations for these compounds are given in Figures 1 and 4. From these variations of intensities with concentrations, we suggest that these ions are formed from $\text{C}_5\text{H}_{11}^+$ as an initial precursor by reactions analogous to reactions 9 and 10. For example, in $t\text{-C}_5\text{H}_{11}\text{SH}$ an ion of high intensity appears at m/e 175 and one of moderate intensity appears at m/e 141. We suggest the reaction sequence



Similarly, in $t\text{-C}_5\text{H}_{11}\text{Br}$ we suggest



The role of $\text{C}_5\text{H}_{11}^+$ as precursor for these ions is supported by the fact that the sum of the intensities of the alkyl ions in the $t\text{-C}_5\text{H}_{11}\text{Br}$ system ($\text{C}_5\text{H}_{11}^+ + \text{C}_6\text{H}_{13}^+$

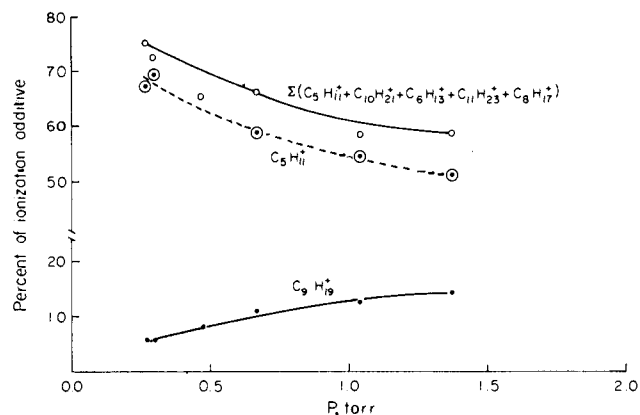


Figure 3. The relative intensities of the $\text{C}_9\text{H}_{19}^+$ ion and the $\text{C}_5\text{H}_{11}^+$ ion (plus ions which are products of reactions of $\text{C}_5\text{H}_{11}^+$) in an $i\text{-C}_4\text{H}_{10}\text{-}t\text{-C}_5\text{H}_{11}\text{Br}$ (1:0.0004) mixture as a function of the total pressure in the reaction chamber at 350°K.

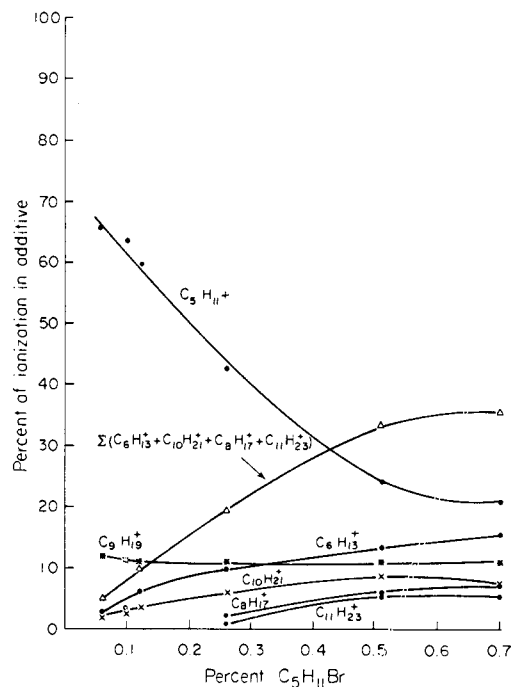


Figure 4. The relative intensities of selected product ions formed in various isobutane- $t\text{-C}_5\text{H}_{11}\text{Br}$ mixtures at a total pressure of 0.74 Torr and 350°K.

$+ \text{C}_{10}\text{H}_{21}^+ + \text{C}_{11}\text{H}_{23}^+$) remains constant as the concentration of $t\text{-C}_5\text{H}_{11}\text{Br}$ is varied. This is the behavior to be expected for ions connected by a reactant-product relationship.

The experiments carried out with $i\text{-C}_4\text{D}_{10}$ as reactant gas generally confirmed and corroborated the proposed mechanisms for the formation of $\text{C}_{10}\text{H}_{21}^+$, $\text{C}_6\text{H}_{13}^+$, and $\text{C}_{11}\text{H}_{23}^+$. That is, in $t\text{-C}_5\text{H}_{11}\text{OH}$, where the formation of $\text{C}_5\text{H}_{10}\text{D}^+$ ions is negligible (Table IV), these products of further reactions of the $\text{C}_5\text{H}_{11}^+$ ion with $t\text{-C}_5\text{H}_{11}\text{OH}$ are all nondeuterated. On the other hand, in $t\text{-C}_5\text{H}_{11}\text{Br}$, where about half of the product *tert*-pentyl ions contain a deuterium atom, one observes $\text{C}_{10}\text{H}_{20}\text{D}^+$ and $\text{C}_{10}\text{H}_{21}^+$ in a ratio of 43:57 and $\text{C}_6\text{H}_{12}\text{D}^+$ and $\text{C}_6\text{H}_{13}^+$ in a ratio of 44:56. (See Table IV.)

Other Observations. The results given in Table III show that at very high additive concentrations ($\geq 0.3\%$) ions of masses corresponding to $\text{C}_8\text{H}_{18}\text{X}^+$ appear.

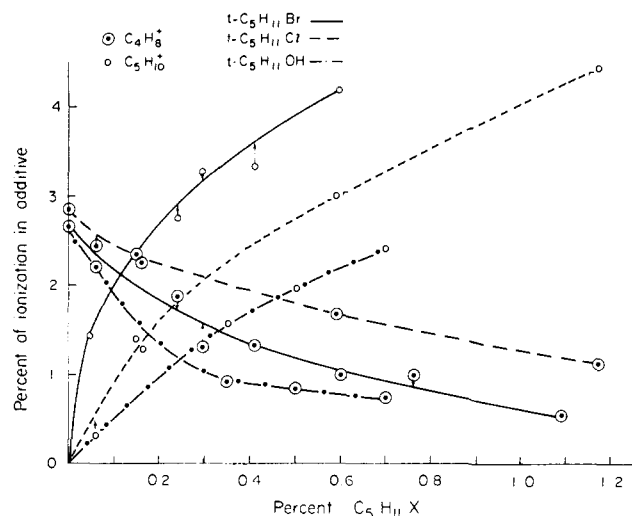
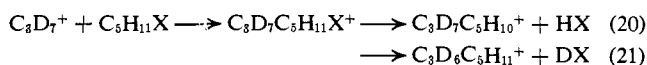


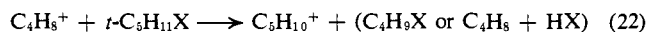
Figure 5. The relative abundances of $C_4H_8^+$ (⊙) and $C_5H_{10}^+$ (○) in isobutane containing $C_5H_{11}Br$ (—), $C_5H_{11}Cl$ (---), and $C_5H_{11}OH$ (-·-) at a total pressure of 0.7 Torr and 350°K.

This is accompanied by the observation of the $C_8H_{17}^+$ ion, suggesting the occurrence of a reaction involving the propyl ion analogous to the displacement reactions 9 and 18. Such a reaction should not be observed except at very high concentrations of the additive compound, since the intensity of $C_3H_7^+$ ions in isobutane at a pressure of about 1 Torr is only a few per cent of the total ionization. A rough estimate indicates that about 5% of the propyl ions initially formed in the system could be intercepted by a reactive additive present in the reaction chamber at a concentration of 1%. In the results presented here, it is thus not surprising that small amounts of ions clearly traceable to propyl ion reactions were observed when the concentration of additive was about 0.3% or higher. Similar results were obtained in the experiments with $i-C_4D_{10}$. In $t-C_5H_{11}Br$, $t-C_5H_{11}OH$, and $t-C_5H_{11}SH$ it was found that the $C_8H_{17}^+$ analogs $C_3D_7C_5H_{10}^+$ and $C_3D_6C_5H_{11}^+$ formed in the sequence



only appeared when the concentration of $t-C_5H_{11}X$ was above about 0.3% in the reaction chamber.

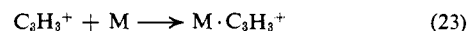
The results given in Tables II and III show that the $C_5H_{10}^+$ ion is important under all conditions in these systems. The mode of formation of this ion is not known. A plausible reaction leading to the formation of $C_5H_{10}^+$ might be



When X is Br, the reaction leading to the formation of butyl bromide as a neutral product is about 20 kcal/mol exothermic. The $C_4H_8^+$ ion comprises 2–3% of the ionization in pure isobutane at pressures of about 1 Torr. Figure 5 shows that the $C_4H_8^+$ ion does diminish in abundance as the concentration of additive $C_5H_{11}Br$, $C_5H_{11}Cl$, or $C_5H_{11}OH$ is increased in isobutane, indicating that $C_4H_8^+$ is reacting. The figure also

shows the increase in the abundance of $C_5H_{10}^+$ with concentration of additive. It is obvious that the maximum yield of $C_5H_{10}^+$ is much greater than the depletion of $C_4H_8^+$, indicating that reaction 22, if it occurs, is not the major mode of formation of $C_5H_{10}^+$. Thus, we cannot account for the formation of most of the $C_5H_{10}^+$ ions observed.

Chemical ionization mass spectra carried out in isobutane reactant gas often show ions corresponding to the addition to the additive compound of the $C_3H_3^+$ ion, an ion formed in small amounts in isobutane



The results given in Table II show that in these mixtures, even at low additive concentrations, the $C_8H_{13}^+$ ion is observed. This is the ion which would be observed if the reaction of $C_3H_3^+$ with $t-C_5H_{11}X$ resulted in the displacement of an HX molecule. The deuterium labeling experiments provide evidence that the $C_8H_{13}^+$ ion does originate in such a displacement reaction. When the $C_3D_3^+$ ion reacts with $t-C_5H_{11}X$, the only analog of $C_8H_{13}^+$ which is observed is $C_3D_3C_5H_{10}^+$.

Conclusions

In this study, we have shown that when a carbonium ion such as $t-C_4H_9^+$, $C_5H_{11}^+$, or $C_6H_{13}^+$ encounters a molecule of $t-C_5H_{11}Cl$, $t-C_5H_{11}Br$, $t-C_5H_{11}OH$, or $t-C_5H_{11}SH$, the most probable reaction is a condensation resulting in the formation of a $C_7H_{2n+1}C_5H_{11}X^+$ ion. This ion is observed in all systems, but the abundances are negligible except in $t-C_5H_{11}SH$. The condensation ions undergo a dissociation to eliminate an HX molecule. In the case of the reactions of $t-C_4H_9^+$, the major product ion observed is actually $C_5H_{11}^+$, which is probably formed by the dissociation of the $C_9H_{20}X^+$ condensation ion.

We have shown that proton transfer from the *tert*-butyl ion to the $t-C_5H_{11}Cl$, $t-C_5H_{11}Br$, and probably $t-C_5H_{11}OH$ molecules is endothermic, and proton transfer to $t-C_5H_{11}SH$ from $t-C_4H_9^+$ is at best only slightly exothermic. The fact that the displacement reactions are important between these pairs suggests that such reactions may be of importance when competing particle transfer reactions are not very energetic. This is in agreement with observations reported from earlier studies,^{6,7} where it was seen that the ethyl ion transfers a proton to all ethyl halides but undergoes competing displacement reactions only with ethyl chloride and ethyl fluoride, for which the proton transfer reaction is close to thermoneutral. The experiments with deuterated isobutane reported here indicate that in $t-C_5H_{11}SH$, where proton transfer possibly does occur, an "internal" proton transfer occurs in the condensation ion which is the precursor to displacement, which thus has the structure $C_9D_8H_{11}SHD^+$. In the molecules where proton transfer is endothermic, there is evidence that the major structure of the condensation ion is one in which no proton rearranges to the site of the halogen atom or -OH group.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation.