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An Ion Cyclotron Resonance Study of the Structures of $C_7H_7^+$ Ions

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Abstract: The $C_7H_7^+$ fragment ions formed in toluene, and the chlorinated, brominated, and iodinated toluenes, as well as the $C_7H_6F^+$ fragment ions in fluorinated toluenes have been studied in an ion cyclotron resonance spectrometer. In all these systems, it is seen that there are two populations of $C_7H_7^+$ ions, one of which reacts with the parent compound and other compounds, and one of which is totally unreactive. Because the reactive $C_7H_7^+$ ions from the different precursors all undergo the same reactions and at the same rate as the $C_7H_7^+$ ions in toluene and benzyl chloride, which have previously been shown to have the benzyl structure, this structure is assigned to the reactive $C_7H_7^+$ populations; the unreactive $C_7H_7^+$ ions are assigned the tropylium structure. The relative abundance of the unreactive tropylium ion is low (<15%) in the chloro-, bromo-, and iodotoluenes, and decreases with decreasing energy of the ionizing electrons. This is interpreted to mean that the rearrangement to the seven-membered ring structure occurs after the fragment ion is formed. In toluene and fluorotoluenes, the unreactive component comprises 30–60% of the $C_7H_6X^+$ ($X = H, F$) ions, and decreases with increasing energy of the ionizing electrons, indicating that rearrangement occurs prior to the fragmentation of the parent ion. Rate constants for the hydride transfer to the benzyl ion from cyclopentane, cyclohexane, 3-methylpentane, and 3-methylhexane are reported. An estimate that $\Delta H_f(C_6H_5CH_2^+) = 219 \pm 4$ kcal/mol is based on the assumption that the maximum endothermicity of reaction is given by $-RT \ln k_{Rn}/k_{\mathrm{collision}}$, as well as on determinations of equilibrium constants for the reactions $C_6H_5CH_2^+ + (CH_3)_3CX \rightleftarrows (CH_3)_3C^+ + C_6H_5CH_2X$ where X = Br or Cl. The relative abundances of benzyl and tropylium ions determined by this technique in various compounds are compared with analogous results from collisional activation spectra. Tolyl ions, if formed, rearrange to the more stable benzyl ion structure within 10^{-3} s.

A number of studies have examined the structures of $C_7H_7^+$ ions formed in various aromatic compounds,[1] and have presented evidence that these ions exist in the gas phase with two or more discrete structures one of which is the tropylium as suggested by Meyerson and coworkers[1a,b] in 1957. This conclusion has been based on several types of experimental observations, some of which will be discussed here.

For example, in high-pressure mass spectrometric studies,[2,3] it has been seen that $C_7H_7^+$ ions of unspecified structure react with toluene to form $C_8H_9^+$ and $C_{14}H_{15}^+$ ions:

$$C_7H_7^+ + C_6H_5CH_3 \rightarrow C_{14}H_{15}^+ \qquad (1a)$$

$$\rightarrow C_8H_9^+ + C_6H_6 \qquad (1b)$$

In both of these studies, a small fraction of the $C_7H_7^+$ ions were unreactive.

More recently, using an ICR spectrometer, Dunbar also observed that the $C_7H_7^+$ ions generated in toluene consist of two populations,[4] distinguishable by their reactivity toward toluene, and pointed out that the two populations probably represent ions of two different structures.[4,5] By studying the reaction analogous to (1b) in partially deuterium-labeled toluenes, $C_6H_5CD_3$ and $C_6D_5CH_3$, Shen et al.[5] were able to demonstrate that the product $C_8(H,D)_9^+$ ion contains three hydrogens from the methyl group of the neutral toluene reactant, four from the ring of the neutral toluene, and two from the $C_7(H,D)_7^+$ reactant with some preference to the hydrogens on the methyl group. From this result they surmised that the reactive $C_7H_7^+$ species has the benzyl structure.

In studies from that laboratory,[4,5] the hypothesis was adopted that the nonreactive $C_7H_7^+$ component has the tropylium structure; the other possible structures, the tolyl ion structures, were considered unlikely because they are known to be higher energy ions.[4,6]

More quantitative results have shown that the reactive $C_7H_7^+$ ion formed in benzyl chloride has the benzyl structure. Abboud et al.[6] determined the equilibrium constant for the

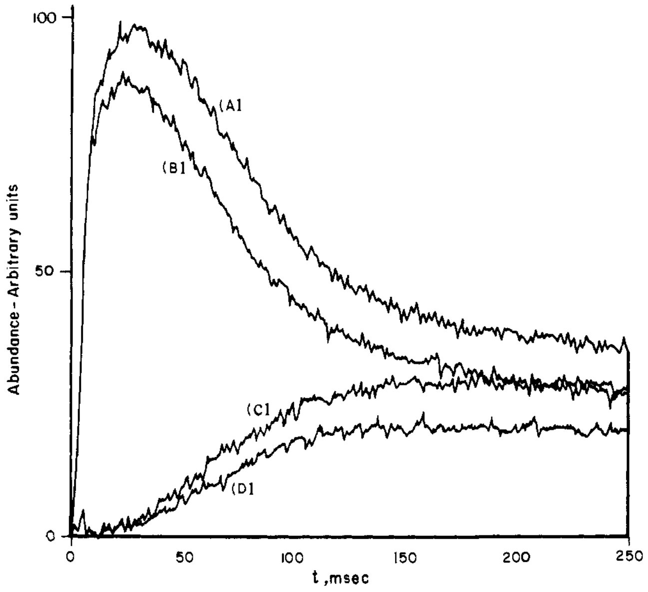


Figure 1. The relative abundances of $C_7D_7^+$ (A) and $C_7H_7^+$ (B) ions formed in $C_6H_5CH_3$-$C_6D_5CD_3$ (1:1), as a function of time. Also shown are the products of the reaction of $C_7D_7^+$ (C) and $C_7H_7^+$ (D) with $C_6H_5CH_3$. The rate constant for the reaction is 1.6 ± 0.1 × 10^{-10} cm^3/molecule s.

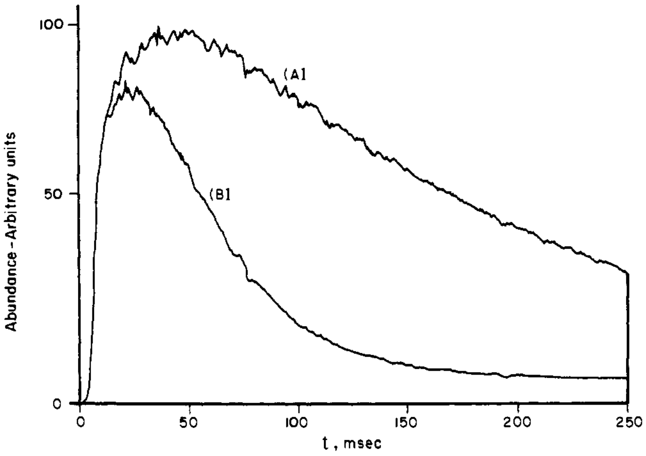


Figure 2. The time dependence of the relative abundance of $C_7H_7^+$ ions generated in *p*-bromotoluene in (A) pure *p*-bromotoluene and (B) in a *p*-bromotoluene-*p*-diethylbenzene (5:1) mixture.

reaction

$$C_7H_7^+ + (CH_3)_3CCl \rightleftarrows (CH_3)_3C^+ + C_6H_5CH_2Cl \quad (2)$$

at 303 and 408 K, and showed that the entropy change for this reaction is inconsistent with a tropylium structure for the reactant ion, whereas the measured ΔH for the reaction is inconsistent with a tolyl ion structure, but consistent with a benzyl structure.

McLafferty and co-workers[7-9] examined the collisional activation spectra of $C_7H_7^+$ ions from a variety of organic compounds. In this technique, relative abundances of different structural isomers are deduced from *m/e* 74 ($C_6H_2^+$), 75 ($C_6H_3^+$), 76 ($C_6H_4^+$), and 77 ($C_6H_5^+$) ions in the fragmentation spectra of $C_7H_7^+$. According to this set of results, the $C_7H_7^+$ ions from substituted toluenes may exist on a time scale of 10^{-5} s in as many as five different structures; the unreactive fraction may include the tolyl ions.

The present study is a systematic examination of the reactivities of the $C_7H_7^+$ ions generated in toluene and a number of substituted toluenes, and an interpretation of the results in terms of the structures of the ions. From the variations in the apparent abundances of the isomeric structures with energy, inferences will be made about the nature of the isomerization reactions.

Experimental Section

The NBS pulsed ion cyclotron resonance spectrometer has been described in detail elsewhere.[10] The experimental and computational procedures followed in deriving reaction rate constants and equilibrium constants have also been discussed previously.[10,11]

In this study, reactions of a particular isomer are studied in the presence of an unreactive ion of the same mass. Thus, it was necessary to determine the reaction rate constants under conditions such that the relative abundance of the unreactive component was known. This could be accomplished by observing the ion in question in the presence of a reactive compound (the parent compound or an additive) for times long enough that all reactive species have disappeared and the abundance of the unreactive component can be observed directly. At the pressures used in this study (10^{-6}–10^{-5} Torr) the ions usually had to be observed for 200–300 ms in order to accomplish this. Since the reactive isomers also undergo reaction with the various parent compounds, the determination of the rate constant for reaction with a foreign compound requires that the rate constant for reaction with the parent compound be known.

$$-\ln I/I_0(t^{-1}) = k_1P_1 + k_2P_2 \qquad \text{(I)}$$

(where P_1 and P_2 represent the number of molecules/cm^3 of the parent compound and the reactive additive, respectively, and k_1 and k_2 are the rate constants for reaction of the $C_7H_7^+$ with the respective compounds).

In practice, for increased accuracy, each rate constant determination was preceded by a measurement of the rate of decay of the ion in its parent compound under the same conditions used for the actual rate constant determination.

Results and Discussion

Figure 1 shows an experimental plot of the abundance of $C_7H_7^+$ and $C_7D_7^+$ as a function of time in a $C_6H_5CH_3$-$C_6D_5CD_3$ mixture in the pulsed ion cyclotron resonance spectrometer. It can be seen that, as described above, a fraction of the $C_7H_7^+$ ($C_7D_7^+$) fragment ions react with toluene, but when these have all disappeared by reaction, a residue of unreactive $C_7H_7^+$ ($C_7D_7^+$) species remains. The relative abundances of the two fractions can readily be discerned from plots such as Figure 1, provided that reaction is slow enough that few ions disappear by reaction during the pulse. Dunbar[4,5] has also used this technique for estimating the relative abundances of these structural isomers.

Analogous plots of $C_7H_7^+$ ions generated in chlorine-, bromine-, iodine-, or nitro-substituted toluenes in the presence of added *p*-diethylbenzene or toluene also have shapes which indicate the presence of a reactive and an unreactive fraction of ions as illustrated in Figure 2. The *p*-diethylbenzene is added because the reactions with the parent compounds are slow (k_{Rn} < 1 × 10^{-10} cm^3/molecule s) so the addition of a molecule which reacts more efficiently simplifies the determination of the relative abundances of the reactive and unreactive isomers. In the absence of such an additive, the disappearance of the reactive component is too slow to observe the unreactive component within 200–300 ms, as can be seen in Figure 2. When the rate constants for reaction of the $C_7H_7^+$ ions from different precursors with a given additive are determined, it is seen that the same value is obtained. This is illustrated in Table I for reactions of $C_7H_7^+$ ions from toluene, and chlorinated, brominated, and iodinated toluenes with several compounds.

As described in the introduction, isotopic labeling experiments have led to the identification of the benzyl ion as the reactive $C_7H_7^+$ species in toluene.[5] Similarly, measurements of the equilibrium constant of reaction 2 led to the conclusion that the $C_7H_7^+$ ion generated in benzyl chloride has the benzyl

Table I. Rate Constants for Reactions of Benzyl Ions from Different Sources with Various Compounds[a]

Source of $C_7H_7^+$	$k_{Rn} \times 10^{10}$, cm^3/molecule s, for reactant molecule				
	p-$(C_2H_5)_2C_6H_4$	c-C_5H_{10}	c-C_6H_{12}	$(C_2H_5)_2CHCH_3$	$CH_3CH_2CH(CH_3)C_3H_7$
$C_6H_5CH_3$	8.2				
$C_6H_5CH_2Cl$	8.8	0.25	0.58	0.81	1.00
o-$C_6H_4ClCH_3$	8.3				
m-$C_6H_4ClCH_3$	9.0	0.27	0.68	0.90	0.95
p-$C_6H_5ClCH_3$	8.2				
$C_6H_5CH_2Br$	8.7	0.27	0.51	0.99	1.19
o-$C_6H_4BrCH_3$	8.7				
m-$C_6H_4BrCH_3$	8.7				
p-$C_6H_4BrCH_3$	8.3				
o-$C_6H_4ICH_3$	7.4	0.26	0.55	0.94	0.95
m-$C_6H_4ICH_3$	8.2				
p-$C_6H_4ICH_3$	8.1				

[a] Error limits: ±15%.

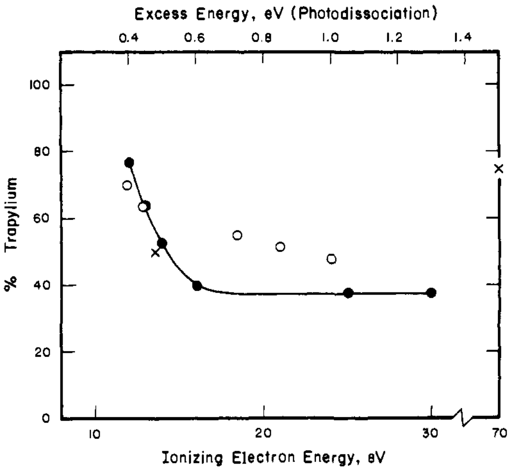


Figure 3. The effect of ionizing electron energy on the relative abundance of the unreactive (tropylium) $C_7H_7^+$ ion in toluene, as derived from the results of this study (●) (error limits ±10%). Also shown are the abundances of the tropylium ions observed by Fu et al. (ref 12) as a function of the excess energy imparted to the $C_7H_8^+$ ions in photodissociation (○, energy scale on top), and the analogous abundances reported by McLafferty et al. (ref 7-9) from collisional activation spectra (x).

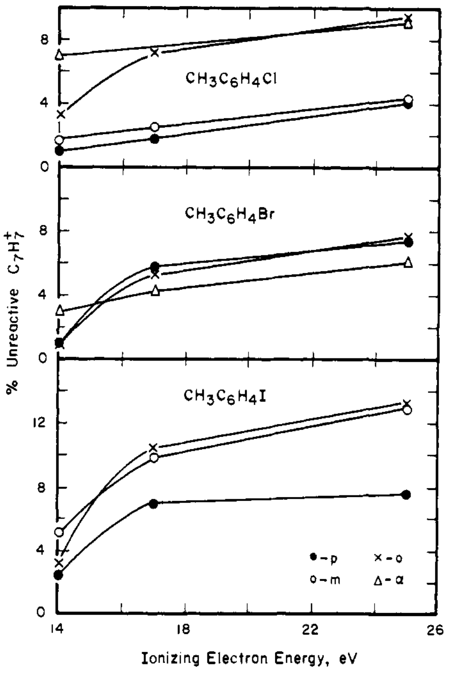


Figure 4. The effect of ionizing electron energy on the relative abundance of the unreactive (tropylium) $C_7H_7^+$ ion in o- (x), m- (○), and p- (●) chloro-, bromo-, and iodotoluenes, as well as in the benzyl (Δ) halides (error limits ±10%).

structure.[6] Since the reactive $C_7H_7^+$ ions generated in all the precursor compounds listed in Table I react with additives with rate constants which are the same within experimental error as those of the benzyl ions formed in toluene and benzyl chloride, it can be concluded that in all these systems, the reactive $C_7H_7^+$ has the benzyl structure. Additional verification of this point was obtained in some isotopic labeling experiments. In a mixture of $C_6H_5CH_3$ and $C_6D_5CD_3$, it was seen that the $C_6H_5CH_2^+$ ion reacts with $C_6D_5CD_3$ to form $C_8D_7H_2^+$ (Figure 1):

$$C_6H_5CH_2^+ + C_6D_5CD_3 \rightarrow C_8D_7H_2^+ + C_6H_5D \quad (3)$$

and that the $C_6D_5CD_2^+$ ion reacts with $C_6H_5CH_3$ to form $C_8H_7D_2^+$. When deuterated toluene was added to the other precursor compounds studied here, the reactive $C_7H_7^+$ component reacted to give a $C_8D_7H_2^+$ product.

It could be seen in these experiments that the reactive fractions of $C_7H_7^+$ apparently did not include additional isomers, since the rate of exponential decay of the reactive ions, corrected for the presence of unreactive ions, in no case varied with observation time. The presence of an isomer reacting at a different rate would be seen as an apparent slowing of the rate of reaction with increasing time as the more reactive component is depleted.

As suggested before, the most probable identity of the unreactive $C_7H_7^+$ species is the tropylium ion; it is unlikely that the less stable tolyl ions would survive without rearrangement on the time scale of these experiments (~10^{-3}-10^{-1} s). This is supported by the fact that when an alkane is added to any of these compounds, the relative abundances of the reactive and unreactive $C_7H_7^+$ components do not change compared to the relative abundances in the pure compound or in the presence of added toluene or p-diethylbenzene. That is, hydride transfer from alkanes to tolyl ions is highly exothermic and would be expected to occur if tolyl ions were present.

The fraction of the $C_7H_7^+$ ions observed in the unreactive (tropylium) structure in toluene and the various halogenated toluenes are shown respectively in Figures 3 and 4 as a function of the energy of the ionizing electrons. There is a sharp contrast between the results shown in the two figures. For a given halogenated toluene compound, the relative abundance of the tropylium ion is generally low (<15%), and decreases with a decrease in the energy of the ionizing electrons (Figure 4), while in toluene, the probability that $C_7H_7^+$ has the tropylium structure is much higher (>30%) but increases as the ionizing energy decreases.

Table II. Relative Abundances of $C_7H_7^+$ Structural Isomers from Aromatic Compounds

Precursor compd	Ionizing electron energy,[a] eV	This work Benzyl	 Tropylium	Collisional activation[b] Benzyl	 Tropylium
Toluene	12-14	23	77	50	50
	25-70	62	38	25	75
Benzyl chloride	25-70	91	9	45	55
p-Chlorotoluene	25-70	96	4	30	70
Benzyl bromide	25-70	94	6	50	50
p-Bromotoluene	25-70	93	7	30	70
p-$CH_3C_6H_4OCH_3$	25-70	71	29	20	80
p-Diphenylethane	25-70	95	5	50	50
2,5-Norbornadiene	25-70	30	70	25	75

[a] This work, 25 eV. Collisional activation experiments, 70 eV. It was verified in several experiments that the observed abundances of the structural isomers did not vary as a function of energy above 25 eV. [b] Reference 8.

Table III. Relative Abundances of $C_7H_7^+$ Structural Isomers from Aromatic Compounds

Precursor compd	Ionizing electron energy,[a] eV	This work Benzyl	 Tropylium	Collisional activation[b] Benzyl	 Tropylium	 Tolyl
o-Iodotoluene	10-14	96	4	25	0	75
	25-70	87	13	0	5	95
m-Iodotoluene	12-14	94	6	5	10	85
	25-70	87	13	0	30	70
p-Iodotoluene	12-14	97	3	35	35	30
	25-70	92	8	0	5	95
m-Nitrotoluene	25-70	60	40	0	35	65

[a] This work, 25 eV. Collisional activation experiments, 70 eV. It was verified in several experiments that the observed abundances of the structural isomers did not vary as a function of energy above 25 eV. [b] Reference 9.

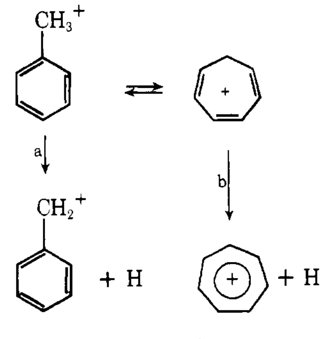
Results obtained in this study by observing the relative abundances of reactive and unreactive $C_7H_7^+$ components may be compared with the relative abundances of the various $C_7H_7^+$ structural isomers in analogous systems as calculated from their collisional activation spectra (Tables II and III). The agreement between the results obtained by the two techniques is generally very poor. The relative abundance of the benzyl ion is underestimated in the collisional activation spectra. The collisional activation spectra are obtained from ions that have survived 10^{-5} s, while the reactivities of the ions are observed after 10^{-3}-10^{-1} s. However, if this difference in the observation time were the only reason for the disagreement between the two sets of results, one would have to rationalize why the abundance of ions in the rearranged tropylium structure is greater at 10^{-5} s than at 10^{-3}-10^{-1} s in compounds such as benzyl chloride or benzyl bromide where most of the $C_7H_7^+$ ions originate in the benzyl structure.

In a number of compounds, notably the iodotoluenes and nitrotoluenes, it has been reported[9] that the $C_7H_7^+$ ions which remain after the benzyl ions have been removed from the system through reaction 1 have collisional activation spectra which are different from the spectrum attributed to the tropylium ion. This is interpreted as evidence for the presence of ions having the tolyl structures. The reported distributions of the benyl, tropylium, or tolyl ion structures from these experiments are listed in Table III, along with the corresponding abundances of the reactive (benzyl) and unreactive (tropylium) structures observed in this investigation. In order to rationalize the differences between these two sets of results in an approximate way, it would be necessary to assume that all the tolyl ions present after 10^{-5} s rearrange exclusively to the benzyl structure within 10^{-3} s, and that (except in *o*-iodotoluene) some of the tropylium ions present at 10^{-5} s rearrange to the benzyl structure as well.

Isomerization Processes in Toluene. The trends with energy observed in toluene are in qualitative agreement with the data reported by Dunbar[12] (Figure 3), who examined the relative abundances of tropylium and benzyl ions formed in the dissociation of toluene parent ions photolyzed by photons of varying energy:

$$C_7H_8^+ + h\nu \rightarrow C_7H_7^+ + H \tag{4}$$

The trend with energy observed (Figure 3) was interpreted to mean that the isomerization process resulting in the eventual formation of the seven-membered ring actually occurs before $C_7H_8^+$ dissociates to $C_7H_7^+$. It was suggested that there is an equilibrium between the toluene and cycloheptatriene structures, each of which may dissociate to give a fragment ion having the corresponding six- or seven-membered ring structure (eq 5). Dunbar[4] suggested that the mechanism favored



(5)

tropylium ion formation because of a lower activation energy for dissociation 5b, and that the decrease in the abundance of the tropylium ion at higher energies reflected the inability of the system to reach equilibrium when the dissociative lifetime of $C_7H_8^+$ was lowered. McLafferty and Winkler[8] also suggested that $C_7H_8^+$ ions formed in toluene equilibrate between the toluene and cycloheptatriene structures, in order to explain their observation that the collisional activation spectra of $C_7H_7^+$ from toluene and from cycloheptatriene are essentially the same. Results based on the collisional activation spectra,[8] however, seemed to indicate that the abundance of the tropylium ion generated in toluene increases, rather than decreases, with increasing energy (Figure 3 and Table II). This was explained by postulating a "looser activated complex" for dissociative 5b than for 5a.

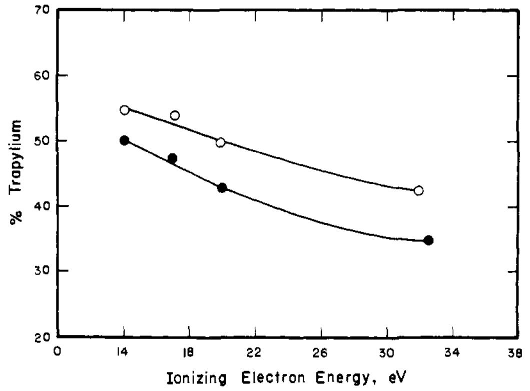


Figure 5. The percentage of the $C_7(H,D)_7^+$ ions from $C_6H_5CD_3$ observed in the unreactive (tropylium) structure, as a function of ionizing electron energy: ○, $C_7H_4D_3^+$; ●, $C_7H_5D_2^+$ (error limits ±10%).

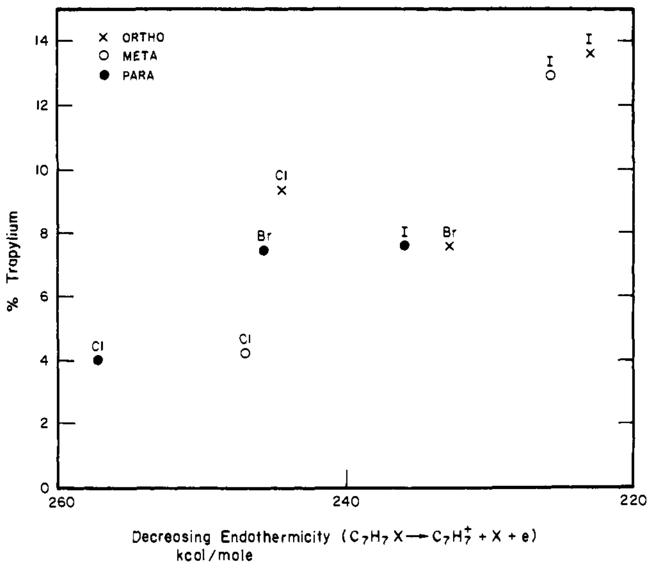


Figure 6. The percentage of $C_7H_7^+$ ions from o- (x), m- (○), and p- (●) halotoluenes observed in the unreactive (tropylium) structure, as a function of the endothermicity of the process $C_7H_7X + e \rightarrow C_7H_7^+ + X + 2e$ (assuming that the initial structure of $C_7H_7^+$ is just that which would result from a simple C-X bond rupture in the original molecule). The energy of the ionizing electrons was 25 eV. Relative reaction enthalpies estimated from thermochemical data in ref 18 and 22.

More detailed information about these processes can be derived from the results shown in Figure 5, which gives the percentage of the unreactive fragment ions observed in $C_6H_5CD_3$ as a function of the energy of the ionizing electrons. In this compound, the $C_7(H,D)_7^+$ ions may be formed by the loss of an H or a D atom from the parent ions:

$$C_7H_5D_3^+ \rightarrow C_7H_5D_2^+ + D \qquad (6a)$$

$$\rightarrow C_7H_4D_3^+ + H \qquad (6b)$$

If a fraction of the fragment ions is formed in a fast dissociation of parent ions which have not undergone any scrambling or rearrangement, then one might expect that the $C_7H_5D_2^+$ ions would have a greater probability of being observed in the reactive (benzyl) structure (i.e., a lower probability for the tropylium structure) than the $C_7H_4D_3^+$ ions, as a result of the occurrence of the process

$$C_6H_5CD_3^+ \rightarrow C_6H_5CD_2^+ + D \qquad (7)$$

The results given in Figure 5 indicate that this is indeed the case, and show that, as one would expect, the probability of the occurrence of process 7 increases with increasing energy. These results essentially confirm that the isomerization resulting in the formation of a seven-membered ring structure does involve the precursor $C_7H_8^+$ ion rather than the fragment $C_7H_7^+$ ion. Corroborative evidence for this isomerization mechanism is given by the fact that the percentage of tropylium ion observed in $C_6D_5CD_3$ is 10% greater under all conditions than the corresponding percentage in $C_6H_5CH_3$ (Figure 1). The dissociative lifetime of the deuterated parent ion is expected to be somewhat longer than that of the undeuterated ion, and therefore, it is reasonable that the isomerization to a seven-membered ring structure should compete with dissociation somewhat more effectively in $C_6D_5CD_3^+$ than in $C_6H_5CH_3^+$.

From the results obtained here, no direct evidence can be obtained bearing on the question of whether isomerization proceeds in both directions, i.e., whether there is an equilibrium between the toluene ion and cycloheptatriene ion at low energies. (Using the techniques of this study, it is difficult to obtain quantitative information about the structures of $C_7H_7^+$ fragment ions in cycloheptatriene, because tropylium ions are produced by an ion-molecule reaction in that system.)

Isomerization Processes in Chloro-, Bromo-, and Iodotoluenes. As shown in Figure 4, in the Cl-, Br-, and I-substituted toluenes the abundance of the unreactive (tropylium) $C_7H_7^+$ isomer increases, rather than decreases, with increasing energy. In these compounds, $C_7H_7^+$ ions are formed through cleavage of the C-X bond (where X is Cl, Br, or I) which is weaker than the corresponding C-H bonds in toluene or cycloheptatriene. Apparently the dissociation of the parent ion by loss of a halogen atom:

$$C_7H_7X^+ \rightarrow C_7H_7^+ + X \qquad (8)$$

is fast compared to rearrangement of the parent ion to a halogenated cycloheptatriene structure, and the $C_7H_7^+$ ions are generated initially with benzyl or tolyl structures, depending on the location of the halogen atom in the parent compound. The benzyl or tolyl ions may then rearrange to the unreactive (tropylium) structure with a probability which increases with increasing internal energy of the ion. Fu, Dymerski, and Dunbar[12] were able to distinguish "rearranged" from "unrearranged" parent ions in these compounds by examining their photodissociation spectra. It was concluded that in p-bromotoluene and o-, m-, and p-chlorotoluene fewer than 5% of the parent ions underwent rearrangement prior to dissociation. Results based on metastable ion abundances[13] and studies of fragmentation kinetics[14,15] may also be interpreted to mean that chloro- and bromotoluene[16] or bromo- and iodotoluene[17] parent ions do not rearrange prior to dissociation. In contrast, the photodissociation spectra of Fu et al. indicated that at energies near threshold, as much as 70% of $C_6H_5CH_2Cl^+$ and 35% of $C_6H_5CH_2Br^+$ rearrange prior to dissociation.

It is also interesting to examine the probability that an ion which originates presumably with the o-, m-, or p-tolyl structure by the loss of a halogen atom from a particular position in the molecule will end up with the reactive (benzyl) structure or the unreactive (tropylium) structure. The probabilities of forming the tropylium ion are shown in Figure 6 for the o-, m-, and p-tolyl ions as a function of the endothermicity of the process:

$$C_7H_7X \rightarrow C_7H_7^+ + X + e \qquad (9)$$

for the experiments in which ionization is effected by 25 eV electrons. (The $C_7H_7^+$ structure is taken as that which would result from the initial C-X bond cleavage.) The figure shows that for all the tolyl structures, the probability of forming the tropylium ion increases with decreasing endothermicity, i.e., with increasing internal energy available to the initial $C_7H_7^+$ ion (assuming that the energy transferred upon electron impact

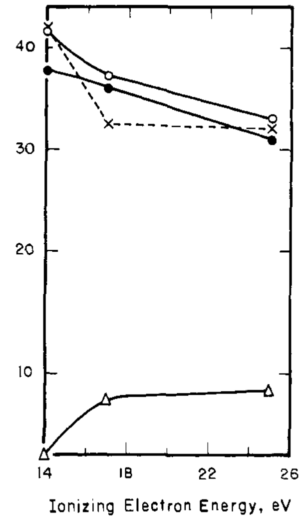


Figure 7. The percentage of $C_7H_6F^+$ ions observed in the unreactive isomeric structure as a function of the energy of the ionizing electrons, in *o*- (x), *m*- (○), and *p*- (●) fluorotoluene, as well as in *p*-fluorobenzyl chloride (△) (error limits ±10%).

Table IV. Thermochemical Data Used in This Study

Species	ΔH_f, kcal/mol[b]	Ref
i-C_4H_{10}	-32.41 ± 0.10	18
$(CH_3)_3CCl$	-43.7 ± 0.6	18
$(CH_3)_3CBr$	-31.88 ± 0.30	18
c-C_5H_{10}	-18.44 ± 0.20	18
c-C_6H_{12}	-29.50 ± 0.15	18
$(C_2H_5)_2CH(CH_3)$	-41.13 ± 0.24	18
$C_6H_5CH_3$	$+11.99 \pm 0.10$	18
$C_6H_5CH_2Cl$	$+4.5 \pm 0.8$	18
$C_6H_5CH_2Br$	$+15.0 \pm 1.2$; 15.1 ± 1.1, $+16.9 \pm 1.8$; 18.6 ± 3.2, $+20.0 \pm 1.1$: Selected value: 16.9 ± 1.8	18
t-$C_4H_9^+$	$+169.1$	21
c-$C_5H_9^+$	$+191$	19
c-$C_6H_{11}^+$	$+174$	19
$(C_2H_6)_2CCH_3^+$	$+155.3$	20[a]
3-$C_6H_{13}^+$	$+168$	19
$C_6H_5CH_2^+$	219 ± 2	This work, see Discussion
c-$C_7H_7^+$	215	22
	195.6	17
	210 ± 5	See Discussion

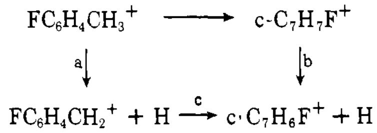
[a] Based on $\Delta H_f(t\text{-}C_4H_9^+) = 169.1$, ref 21. [b] 1 kcal/mol = 41.8 kJ = 0.043 eV.

is identical). Furthermore, the probability of rearrangement to the tropylium structure is, within experimental error limits, the same for an *o*-, *m*-, or *p*-tolyl ion formed with the same internal energy. This latter result indicates that the tropylium ion may be formed through the same intermediate in the three cases.

Isomerization Processes in Fluorinated Toluenes. It is interesting to compare the results given in Figures 3 and 4 with similar results obtained in fluorinated toluenes. In these compounds, in contrast to the other halogenated species discussed here, the C-X bond does not break in the fragmentation of the parent ion:

$$C_7H_7F^+ \rightarrow C_7H_6F^+ + H \qquad (10)$$

The $C_7H_6F^+$ fragment ions show reactive and unreactive fractions analogous to the two fractions observed for the $C_7H_7^+$ ions when reacted with *p*-diethylbenzene and it is reasonable to assume that the $C_7H_6F^+$ ions thus are formed with analogous structures. The relative abundances of unreactive $C_7H_6F^+$ ions formed in *o*-, *m*-, and *p*-fluorotoluene are presented in Figure 7 as a function of the energy of the ionizing electrons. The abundances of the unreactive fragment ions in these compounds decrease with increasing energy. Since this is the same trend as was observed in toluene (Figures 3 and 5), it can be argued by analogy that in the fluorotoluenes, the dissociation of the parent ion is slow enough that rearrangement may occur first:



$$\begin{tikzcd} FC_6H_4CH_3^+ \arrow[r] \arrow[d, "a"] & c\text{-}C_7H_7F^+ \arrow[d, "b"] \\ FC_6H_4CH_2^+ + H \arrow[r, "c"] & c\text{-}C_7H_6F^+ + H \end{tikzcd} \qquad (11)$$

It has been shown before[14-16] that in fluorotoluenes, ring expansion occurs before fragmentation. These results may be compared with analogous results on the same ion, $C_7H_6F^+$, generated in *p*-$FC_6H_4CH_2Cl$. In this compound, it is to be expected that loss of Cl from the parent ion will be fast compared to any rearrangement in the parent ion. Thus, one would predict that the fluorinated tropylium ion observed in this compound would result primarily from rearrangement of fluorinated benzyl fragment ions (path c in reaction 11) rather than from fragmentation of the rearranged molecular ions, c-$C_7H_7ClF^+$, analogous to the c-$C_7H_7F^+$ ions (path b in reaction 11). As shown in Figure 7, the abundance of these unreactive $C_7H_6F^+$ ions increases with increasing electron energy in accord with this prediction.

Heats of Formation of $C_7H_7^+$ Ions. The results given in Table I, showing the rate constants for reaction of the benzyl ion with alkanes and cycloalkanes:

$$C_6H_5CH_2^+ + RH \rightarrow R^+ + C_6H_5CH_3 \qquad (12)$$

can be used to obtain information about the heat of formation of the benzyl ion in the cases where values for the heats of formation of R^+ and RH are available. (A summary of the independent thermochemical information used in this discussion is presented in Table IV. Thermochemical data are given in units of kcal/mol, where 1 kcal/mol = 4.18 kJ = 0.04 eV). If it is assumed that reaction 12 can only be observed if it is exothermic, thermoneutral, or very slightly endothermic, an approximate lower limit can be obtained for $\Delta H_f(C_6H_5CH_2^+)$ from the expression

$$\Delta H \equiv 0 \equiv \Delta H_f(C_6H_5CH_3) + \Delta H_f(R^+) - \Delta H_f(RH) - \Delta H_f(C_6H_5CH_2^+) \qquad (II)$$

Further, another approximation of the lower limit of $\Delta H_f(C_6H_5CH_2^+)$ may be obtained if we assume that the maximum endothermicity can be predicted from the Arrhenius-type relationship when P is assumed to be unity:

$$k_{Rn} = k_{Coll}Pe^{-\Delta H/RT} \qquad (III)$$

(where P is the probability that a collision will lead to reaction when the exponential term approaches unity). The lower limits to $\Delta H_f(C_6H_5CH_2^+)$ predicted from the heats of formation of the relevant RH and R^+ species, and from the measured rate constants and calculated collision rate constants, are listed in Table V. According to these results, the heat of formation of $C_6H_5CH_2^+$ must be at least 221 ± 2 kcal/mol on the basis of the thermochemical data listed in Table III. The value is in good agreement with the recent MINDO calculation[17] of 220.4 kcal/mol, but somewhat higher than the value of 217.2 kcal/mol derived by Abboud, Hehre, and Taft[6] from a determination of the equilibrium constant of reaction 2. Because that equilibrium constant determination did not take into account the presence of a nonreactive fraction of ions, a redetermination was made during the course of this investigation. A value of -0.13 ± 0.03 kcal/mol for $\Delta G°_{300}$ was obtained, in good

Table V. Estimated Minimum Values for the Heat of Formation of the Benzyl Ion

Reaction obsd	k_{Rn}/k_{Coll}[a]	Minimum $\Delta H_f(C_6H_5CH_2^+)$, kcal/mol[b]	
		Assuming $\Delta H_{Rn} = 0$	Assuming $\Delta H_{Rn} = -RT \ln k_{Rn}/k_{Coll}$
$C_6H_5CH_2^+ + (CH_3)_3CH \rightarrow t\text{-}C_4H_9^+ + C_6H_5CH_3$	0.045	213.1	211.2
$C_6H_5CH_2^+ + c\text{-}C_6H_{12} \rightarrow c\text{-}C_6H_{11}^+ + C_6H_5CH_3$	0.080	215.5	214.0
$C_6H_5CH_2^+ + c\text{-}C_5H_{10} \rightarrow c\text{-}C_5H_9^+ + C_6H_5CH_3$	0.024	221.4	219.2
$C_6H_5CH_2^+ + n\text{-}C_6H_{14} \rightarrow C_6H_{13}^+ + C_6H_5CH_3$	0.034	219.9	217.9

[a] Calculated from the Langevin–Gioumousis–Stevenson (ref 23 and 24) formulation. [b] 1 kcal/mol = 4.18 kJ = 0.043 eV.

agreement with Hehre et al.[6] In addition, a value of 8.0 was determined for the equilibrium constant at 300 K of the analogous reaction:

$$C_6H_5CH_2^+ + (CH_3)CBr \rightleftarrows (CH_3)_3C^+ + C_6H_5CH_2Br \qquad (13)$$

which (if one assumes that ΔS for reaction 13 is about the same as that for reaction 2,[6] ~0.5 eu) leads to a value for the enthalpy of reaction 13 of −1.25 ± 0.1 kcal/mol. If one accepts the value for $\Delta H_f(C_6H_5CH_2Br)$ of 16.9 kcal/mol recommended by Cox and Pilcher[18] (experimental determinations of this quantity listed in Table IV vary from 15 to 20 kcal/mol), this result leads to a value for $\Delta H_f(C_6H_5CH_2^+)$ of 219 ± 3, in agreement with the value derived from the results of Table I, but again, higher than the value obtained from the equilibrium constant of reaction 2. However, if we subtract the equation expressing the thermochemical relationships of eq 2 from that of eq 13, it can be shown that

$$\begin{aligned}\Delta H_f(C_6H_5CH_2Br) - \Delta H_f(C_6H_5CH_2Cl) \\ - \Delta H_f(CH_3)_3CBr + \Delta H_f(CH_3)_3CCl \\ = -1.25 + 0.13 \qquad (IV)\end{aligned}$$

$\Delta H_f(C_6H_5CH_2Br) - \Delta H_f(C_6H_5CH_2Cl) = 10.7$ kcal/mol (since heats of formation of $(CH_3)_3CBr$ and $(CH_3)_3CCl$ are well established while those of the benzyl compounds are not[18]). Thus, if one accepts the "recommended" value[18] for $\Delta H_f(C_6H_5CH_2Br)$, one must conclude that the single experimentally determined value of $\Delta H_f(C_6H_5CH_2Cl)$ in the literature is too low by 1.7 kcal/mol. If this correction is made, the value of $\Delta H_f(C_6H_5CH_2^+)$ derived from the equilibrium constant of reaction 2 comes into agreement with that derived from reaction 13; both values are in agreement with the lower limit derived from the results of Table I, and with the value of 220.9 ± 1 determined by Elder and Parr[25] from the photoionization of the benzyl radical.

On the other hand, if we accept the heat of formation of $C_6H_5CH_2Cl$ reported in the literature,[18] then the "recommended" value[18] of $\Delta H_f(C_6H_5CH_2Br)$ is too high (the two determinations which give values of 15 kcal/mol are then correct), and the heat of formation of the benzyl ion must be 217 ± 2 kcal/mol. If one accepts this value, then the values taken for the heats of formation of the alkyl ions formed as products in reaction 12 are too high (again assuming that if reaction 12 is observed, it cannot be more endothermic than would be predicted by eq III). Since the heats of formation of these ions were determined relative to that of $t\text{-}C_4H_9^+$ (ΔH_f = 169.1 kcal/mol),[20] this line of reasoning leads to the conclusion that $\Delta H_f(t\text{-}C_4H_9^+)$ must be lowered to 167.4 kcal/mol.

In view of the large uncertainties in the heats of formation of some of the pertinent species, it is not possible to resolve the discrepancies in the heats of formation of $C_6H_5CH_2^+$, $C_6H_5CH_2Cl$, $C_6H_5CH_2Br$, and the alkyl ions listed in Table III. At the present time, therefore, one can only choose an intermediate value of 219 kcal/mol for the heat of formation of the benzyl ion, and assign wide enough error limits to this and the other heats of formation to accommodate the discrepancies.

The difference in the heats of formation of the benzyl ion and the tropylium ion was recently calculated[6] to be 9.2 ± (2–3) kcal/mol, which would lead to a value for $\Delta H_f(c\text{-}C_7H_7^+)$ of 210 ± 5 kcal/mol. Experimentally, the ionization potential of the cycloheptatrienyl radical has been determined to be 6.24 ± 0.01 eV;[25] the uncertainties in the heat of formation of the tropylium ion are due to the uncertainties in the heat of formation of this radical, which has been estimated to be 64.8[26] or 71.3 kcal/mol.[22] These values lead respectively to values for $\Delta H_f(c\text{-}C_7H_7^+)$ of 209 and 215 kcal/mol, both of which are within the error limits of the value based on the theoretical calculation. A recent critical compilation[22] lists 215 kcal/mol as the preferred value for $\Delta H_f(c\text{-}C_7H_7^+)$, while a MINDO calculations[17] led to a value of 195.6 kcal/mol.

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