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Structure and Isomerization of $C_7H_7^+$ Ions Formed in the Charge-Transfer-Induced Fragmentation of Ethylbenzene, Toluene, and Norbornadiene

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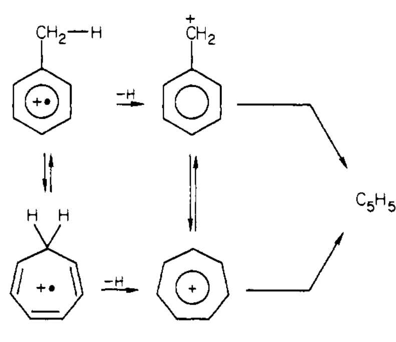
Abstract: $C_7H_7^+$ ions with internal energies varying from ~0.5 to 6.5 eV above their ground-state energy have been prepared in an ion cyclotron resonance spectrometer (ICR) by charge-transfer-induced fragmentation of ethylbenzene, toluene, and norbornadiene. It is shown that in the case of (ethyl-α,α-d_2)benzene and toluene-α,α,α-d_3 the abundance of unscrambled $C_6H_5CD_2^+$ ions produced by direct bond cleavage increases with energy to reach respectively 65 and 10% of the total $C_7(H,D)_7^+$ population at 3 eV above the appearance energy. $C_7H_5D_2^+$ ions are also produced after the occurrence of ring expansion and contraction in the parent ion. However, because these ions produced from (ethyl-α,α-d_2)benzene are not statistically scrambled, especially at high internal energies, it is suggested that only a few passages over the energy barrier separating the six-membered ring from the seven-membered ring structure occur during the dissociative lifetime of the ethylbenzene ion. In contrast, the hydrogens in benzyl-d_2 and benzyl-d_3 ions produced from toluene-α,α,α-d_3 after ring expansion are statistically scrambled. At higher energies, the benzyl ions undergo extensive scrambling, possibly as a result of a fast equilibrium between the benzyl and tropylium ion structures, as proposed in a collisional activation electron-impact study of C_7H_8 compounds by McLafferty and Bockhoff. However, the internal energy at which the $C_7H_7^+$ undergoes isomerization (3–4 eV) in the ICR is higher than that derived from the CA study (~2 eV). With regard to the population of benzyl (B^+) and tropylium (T^+) ions from the three title compounds, it is found that the ratio B^+/T^+ increases with energy to reach a maximum around 3.5 eV above the threshold for formation of T^+. At energies of ~5 eV, B^+/T^+ is seen to decrease with energy. This increased population of tropylium ions occurs in the energy range where hydrogen scrambling of the benzyl ion is observed and where the $C_7H_7^+$ ions undergo extensive fragmentation to produce $C_5H_5^+$. The latter ion exhibits at least two distinct structures.

In an ion cyclotron resonance (ICR) study of the toluene ion, Dunbar clearly showed[1] that an increase in the internal energy of the photodissociating $C_7H_8^+$ ion led to an increase of the abundance of the fragment benzyl ion over that of the isomeric tropylium ion:

$$\begin{aligned} \text{toluene} + h\nu \rightarrow \text{toluene}^{+*} &\rightarrow C_6H_5CH_2^+(B^+) + H \\ &\rightarrow c\text{-}C_7H_7^+(T^+) + H \end{aligned} \qquad (1)$$

In a subsequent ICR study[2] based on the different kinetic behaviors of the two isomers,[2,3] it was similarly found that an increase in electron energy from 11 to 15 eV enhances the probability of producing B^+. In a recent collisional activation (CA) study, McLafferty and Bockhoff[4] confirmed this rise in the percent of B^+ at electron energies from the thermodynamic threshold for the formation of T^+ up to about 15 eV[4]. However, at energies above 16 eV, a reverse in this trend was observed in the CA study (in agreement with an earlier CA study),[5] while in the kinetic ICR study[2] an energy-independent B^+/T^+ ratio was seen in the energy range 15–40 eV.

Scheme I



In view of the fact that in the CA study[4] the B^+/T^+ ratio

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[1] Dunbar, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 1382.

[2] Jackson, J.-A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.

[3] (a) Ausloos, P.; Jackson, J.-A.; Lias, S. G. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 269. (b) Sharma, D. K. S.; Kebarle, P. *Can J. Chem.* **1981**, *59*, 1592.

[4] McLafferty, F. W.; Bockhoff, F. M. *J. Am. Chem. Soc.* **1979**, *101*, 1783.

[5] McLafferty, F. W.; Winkler, J. *J. Am. Chem. Soc.* **1974**, *96*, 5182.

obtained in the electron-impact ionization of cycloheptatriene also exhibited a maximum around 15 eV, Scheme I was proposed.

The increase in the percentage of $C_7H_7^+$ having the benzyl structure from the onset up to an electron energy of 15 eV is ascribed[4] to a fast equilibrium between the excited parent toluene and cycloheptatriene parent ion structures, favoring the former at higher energies, while the falloff at electron energies above 15 eV (where $C_7H_7^+$ is formed with approximately 2 eV in internal energy) is ascribed to a rapid equilibrium between the two $C_7H_7^+$ structures, favoring T^+ at higher electron energies (~20–60 eV). Theoretical calculations[6] predict that the threshold for the $T^+ \rightarrow B^+$ isomerization is about 2.5 eV above the threshold for T^+ formation.

So that the CA data might be reconciled with the ICR observations,[2] it was suggested[4] that the absence of the high-energy falloff of the B^+/T^+ ratio in the ICR study might arise from a displacement of the $B^+ \rightleftarrows T^+$ equilibrium, caused by the preferential removal of the equilibrating B^+ ions through chemical reaction.

In the present study, we examine the $C_7H_7^+$ ions produced in the dissociative charge transfer of toluene, norbornadiene, and ethylbenzene. Ionization of the parent molecule by charge transfer allows us to prepare $C_7H_7^+$ ions with a fairly well-defined internal energy content. It also allows us to extend the internal energy beyond the calculated[4] 2.8 eV average internal energy, which corresponds to $C_7H_7^+$ ions from toluene produced at the highest electron energy (60 eV) achieved in the CA study. In addition, the position of the D atoms in benzyl-d_2 ions originating from toluene-α,α,α-d_3 and (ethyl-α,α-d_2)benzene is determined, in order to shed more light on the proposed $B^+ \rightleftarrows T^+$ equilibrium. Such an equilibrium process would necessarily lead to H–D scrambling in the $C_7H_5D_2^+$ ions prior to reaction. As in previous ICR studies,[2,3] the benzyl ions are distinguished from the tropylium ions through their high reactivity with aromatic molecules.

The results presented here also give information about the expansion and contraction between six- and seven-membered rings involving toluene and ethylbenzene parent ions. It is important to note that these parent ion isomerization processes involve *only* ions that have enough energy to dissociate. It has been shown[7] that $C_7H_8^+$ ions that do not dissociate within 10^{-3} s retain their original structures.

Experimental Section

The NBS pulsed-ion cyclotron resonance spectrometer has been described in detail elsewhere.[8] The operating temperature in the ion source was 335 K, and the pressure of these experiments was 10^{-6}–10^{-5} torr. The abundances of the ions were observed as a function of time for 250–500 ms.

In this study, parent toluene, norbornadiene, and ethylbenzene ions were formed with well-defined energies by charge transfer from various atomic, diatomic, or triatomic ions. The charge donor/hydrocarbon ratio in these experiments was varied from 10 to 50 (total pressure: (1–2) × 10^{-5} torr, nominal electron energy, 60 eV). The decay of the charge donor ion and the growth of the hydrocarbon parent ion were monitored, and the results reported were taken under conditions that the observed direct ionization of the hydrocarbon was 5% or less of the total ionization.

In this study, as in earlier studies carried out in this laboratory,[3a,9] the relative abundances of two isomeric ions (in this case, B^+ and T^+) are determined through differences in their kinetic behavior. That is, a fraction of the $C_7(H,D)_7^+$ ions initially formed disappear by reaction and are identified as B^+; unreactive ions are assigned the T^+ structure. The estimation of the relative abundances of the two isomers from time plots of $C_7(H,D)_7^+$ abundance may tend to underestimate the importance of the reactive (B^+) isomer somewhat, since a small fraction of these ions may react at short times, so that the maximum in the abundance–vs.–time plot does not represent the total abundance of $C_7(H,D)_7^+$ ions initially formed. It is estimated from an observation of the abundance of reaction products as a function of time that the error in the estimated abundance of B^+ from this cause will be less than 10%.

In this study, it was necessary to determine reaction rate constants for B^+ ions under conditions such that the unreactive T^+ ion was present in nonnegligible fractions. This was done by observing the ions for times long enough that the reactive B^+ ions all disappear through reaction, and the abundance of T^+ could be seen and corrected for.

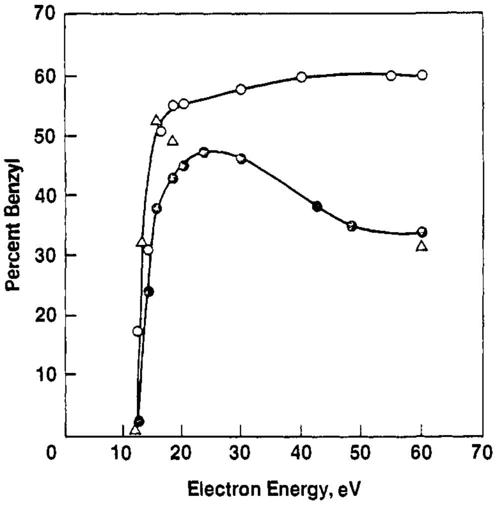

Figure 1. Percentage of $C_7H_7^+$ fragment ions detected in the benzyl structure in the electron-impact-induced fragmentation of toluene (○) and norbornadiene (●) as a function of ionizing electron energy. The toluene collisional activation results from ref 4 are also shown (△). The internal energy of the parent ion is estimated (ref 4) to be ~2 eV at an electron energy of 16 eV and ~2.8 eV at an electron energy of 60 eV.

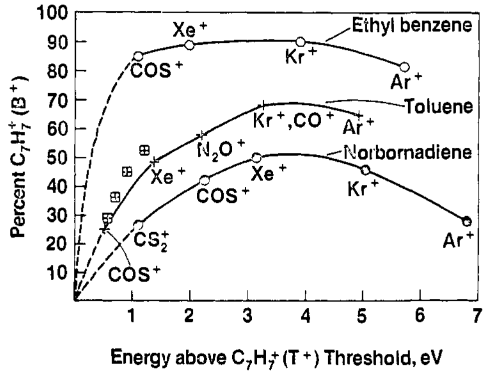

Figure 2. Percentage of $C_7H_7^+$ fragment ions detected in the benzyl structure in the charge-transfer-induced fragmentation of norbornadiene (●), toluene (×), and ethylbenzene (○) as a function of energy above the threshold for tropylium ion (T^+) formation. The charge donors are indicated. Boxed points for toluene are from the photodissociation study (ref 1).

Results

Population of B^+ and T^+ Ions. Figure 1 shows the percent B^+ produced in the electron-impact-induced dissociation of toluene and norbornadiene as a function of electron energy. Experimental points obtained by McLafferty and Bockhoff[4] using the collisional activation (CA) technique on toluene are also included.

Figure 2 shows the percent of benzyl ions formed in the dissociative charge transfer from various charge donors to toluene, norbornadiene, and ethylbenzene. The charge donors and the corresponding recombination energies are as follows: COS^+, 11.2 eV; O_2^+, 12.07 eV; Xe^+, 12.13 eV; N_2O, 12.9 eV; CO_2^+, 13.8 eV; CO^+, 14.0 eV; Kr^+, 14.0 eV; N_2^+, 15.6 eV; Ar^+, 15.76 eV.[10] The

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[6] (a) Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 2446. (b) Cone, C.; Dewar, M. J. S.; Landman, D. *Ibid.* **1977**, *99*, 372.

[7] (a) Dunbar, R. C.; Fu, E. W.; *J. Am. Chem. Soc.* **1973**, *95*, 2716. (b) Hoffman, M. K.; Bursey, M. M. *Tetrahedron Lett.* **1971**, 2539.

[8] Lias, S. G.; Eyler, J. R.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219.

[9] (a) Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1978**, *100*, 7915. (b) Ausloos, P. *Ibid.* **1981**, *103*, 3931.

[10] (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*. (b) Levin, R. D.; Lias, S. G. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1982**, *71*.

abscissa in Figure 2 represents the energy in excess of that required to produce T^+ from these three compounds. The appearance potentials of T^+ from toluene, ethylbenzene, and norbornadiene were taken to be 10.71, 10.06,[11] and 8.95 eV,[12] respectively. The percent B^+ in these experiments is taken as the ratio of reactive $C_7H_7^+$ over the total $C_7H_7^+$ population, determined from tracings such as those given in previous ICR studies[2,3,9] in which the ions are formed by electron impact and charge transfer. The rate constants of the charge-transfer reactions from Ar^+, Kr^+, and Xe^+ to toluene, norbornadiene, and ethylbenzene are within 20% of the calculated collision rate constants. (A similar observation was made for charge-transfer reactions from these ions to other organic compounds.[13]) In the toluene mixtures, the B^+ ions react with toluene to give $C_8H_9^+$:

$$C_7H_7^+(B^+) + C_6H_5CH_3 \rightarrow C_8H_9^+ + C_6H_6 \qquad (2)$$

In ethylbenzene, the following two reactions occur:

$$C_7H_7^+(B^+) + C_6H_5CH_2CH_3 \rightarrow C_9H_{11}^+ + C_6H_6 \qquad (3)$$

$$C_7H_7^+(B^+) + C_6H_5CH_2CH_3 \rightarrow C_6H_5CHCH_3^+ + C_7H_8 \qquad (4)$$

(Ethyl-α,α-d_2)benzene experiments show that the hydride ion transferred in reaction 4 is exclusively from the α position. The reactive $C_7H_7^+$ ions in norbornadiene yield $C_8H_9^+$ in addition to higher molecular weight condensation ions. Addition of toluene-d_8 to norbornadiene yielded $C_8D_7H_2^+$ as a major product, indicating the occurrence of the benzyl ion reaction:

$$C_6H_5CH_2^+ + C_6D_5CD_3 \rightarrow CD_3C_6D_4CH_2^+ + C_6H_5D \qquad (5)$$

Attempts to obtain accurate information on the $C_7H_7^+$ populations from cycloheptatriene were unsuccessful. The main problem was the formation of tropylium ions through the reaction:

$$c\text{-}C_7H_8^+ + c\text{-}C_7H_8 \rightarrow C_7H_7^+ + C_7H_9 \qquad (6)$$

The growth of T^+ as a function of time made it impossible to determine B^+ by monitoring the $C_7H_7^+$ abundance as a function of time.

In all these systems, the unreactive $C_7H_7^+$ ions are assumed to be tropylium (T^+) ions. Although this cannot be demonstrated with certainty, it was verified that these ions are entirely unreactive toward a wide variety of halides, acids, ketones, aldehydes, alcohols, and amines. The rate constant for reaction of B^+ with toluene is $(2.5 \pm 0.3) \times 10^{-10}$ cm^3/(molecule·s), independent of the nature of the charge donor. A rate constant of $(6.5 \pm 0.1) \times 10^{-10}$ cm^3/(molecule·s) was obtained for the disappearance of B^+ by reaction with ethylbenzene, when the ion was generated by charge transfer to ethylbenzene from COS^+, O_2^+, Xe^+, N_2O^+, CO_2^+, CO^+, and Kr^+. However, a slightly lower value [$(5.8 \pm 0.1) \times 10^{-10}$ cm^3/(molecule·s)] was derived for the $C_7H_7^+$ ions produced in the Ar^+-induced fragmentation of ethylbenzene.

In the charge-transfer experiments, the $C_7H_7^+$ ions are stable when formed with up to 4 eV in internal energy. At energies above 4–5 eV, $C_5H_5^+$ is observed. In cycloheptatriene, toluene, α-bromotoluene, and α-chlorotoluene about 95% of the $C_5H_5^+$ fragment ions react rapidly with the parent molecule [$k \sim 10^{-9}$ cm^3/(molecule·s)] while in norbornadiene a considerable fraction of the $C_5H_5^+$ ions are unreactive [$k < 10^{-11}$ cm^3/(molecule·s)]. The unreactive $C_5H_5^+$ population was estimated at 19% in the Kr^+-sensitized fragmentation of norbornadiene and 50% in the Ar^+-sensitized fragmentation.

The Position of the D Atoms in $C_7H_5D_2^+$ from Toluene-α,α,α-d_3 and (Ethyl-α,α-d_2)benzene. Table I shows the ratios of $C_7H_5D_2^+/C_7H_4D_3^+$ ions, obtained in the dissociative charge transfer of toluene-α,α,α-d_3. Also given are the B^+/T^+ ratios for the $C_7H_5D_2^+$ and $C_7H_4D_3^+$ ions produced at the various energies.

Table I. $C_7(H,D)_7^+$ Ions Formed in the Charge-Transfer-Induced Dissociation of $C_6H_5CD_3$

charge donor	$C_7H_5D_2^+/C_7H_4D_3^+$ [b]	B^+/T^+ [a]	
		$C_7H_5D_2^+$	$C_7H_4D_3^+$
Xe^+	0.28	0.77 ± 0.05	0.66 ± 0.05
CO_2^+	0.42	1.60 ± 0.05	1.60 ± 0.05
Kr^+	0.48	2.0 ± 0.1	2.0 ± 0.1
Ar^+	0.66	2.0 ± 0.1	1.6 ± 0.1
statistical	0.60		

[a] The ratio of the designated $C_7(H,D)_7^+$ ions having the benzyl structure to those having the tropylium structure. See Discussion. [b] For a detailed discussion of the isotope effects on H/D loss from $C_6H_5CD_3^+$, see ref 23.

In order to ascertain the number of H/D atoms retained on the methylene group of the benzyl ion, we determined the abundance of the methylene transfer product ions, e.g., in the case of toluene:

$$C_7H_5D_2^+(B^+) + C_6H_5CD_3 \rightarrow CD_3C_6H_4CH_2^+ + C_6H_4D_2 \qquad (7a)$$

$$C_7H_5D_2^+(B^+) + C_6H_5CD_3 \rightarrow CD_3C_6H_4CHD^+ + C_6H_5D \qquad (7b)$$

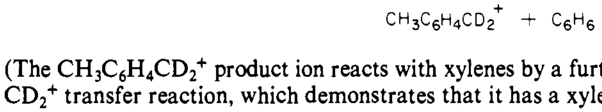
$$C_7H_5D_2^+(B^+) + C_6H_5CD_3 \rightarrow CD_3C_6H_4CD_2^+ + C_6H_6 \qquad (7c)$$

Because these three $C_8(H,D)_9^+$ ions are also produced through analogous reactions involving $C_7H_4D_3^+(B^+)$ ions, the individual reaction channels were sorted out by double resonance ejection of $C_7H_5D_2^+$ and $C_7H_4D_3^+$, respectively. Table II shows the product ion distributions for the benzyl-d_2 and benzyl-d_3 ions, as obtained in such experiments. The statistically expected distribution, assuming complete scrambling in $C_7(H,D)_7^+$ but *no* scrambling in the reaction complex, is given as well.

In order to verify if the methylene transfer reaction occurs without H–D scrambling in the collision complex, we prepared $C_6H_5CD_2^+$ ions by the reaction of CD_2F^+ with benzene:[14]

$$CD_2F^+ + C_6H_6 \rightarrow C_6H_5CD_2^+ + HF \qquad (8)$$

Upon addition of $C_6H_5CH_3$, 90% of the $C_6H_5CD_2^+$ ions reacted to yield $C_8H_7D_2^+$, clearly showing that as suggested before[2,15] the most probable methylene transfer reaction can be written as follows:



(9)

(The $CH_3C_6H_4CD_2^+$ product ion reacts with xylenes by a further CD_2^+ transfer reaction, which demonstrates that it has a xylenyl ion structure.) It is unlikely that H–D scrambling in the complex (reaction 9) will be greater for $C_6H_5CD_2^+$ reactant ions of high internal energy, since the shorter lifetime associated with an energetic complex would lead to a decrease in rearrangements within the complex.

In the electron-impact[16] and charge-transfer-induced fragmentation of (ethyl-α,α-d_2)benzene, the $C_7H_5D_2^+$ ions are produced in the absence of other $C_7(H,D)_7^+$ ions. Therefore, the $C(H,D)_2$ transfer reactions

$$C_7H_5D_2^+(B^+) + C_6H_5CD_2CH_3 \rightarrow CH_3CD_2C_6H_4C(H,D)_2^+ + C_6(H,D)_6 \qquad (10)$$

can be sorted out in the absence of double resonance ejection. The

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(11) McLoughlin, R. G.; Morrison, J. D.; Traeger, J. C. *Org. Mass Spectrom.* **1979**, *14*, 104.

(12) This value is calculated taking a value of 8.89 eV for the heat of formation of the tropylium ion (ref 11) and a value of 2.19 eV for the heat of formation of norbornadiene (Pedley, J. B.; Rylance, J. "N. P. L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex, 1977).

(13) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 6505.

(14) Beauchamp, J. L. In "Interactions between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1975; p 413.

(15) Shen, J.; Dunbar, R. C.; Olah, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 6227.

(16) Venema, A.; Nibbering, N. M. M.; de Boer, T. J. *Tetrahedron Lett.* **1971**, 2141.

Table II. Relative Abundances of Product Ions Formed in Reactions I and II[a]

charge donor	% distribution			$(C_7H_4D_3)CHD^+/(C_7H_4D_3)CH_2^+$
	$(C_7H_4D_3)CD_2^+$	$(C_7H_4D_3)CHD^+$	$(C_7H_4D_3)CH_2^+$	
		Reaction I		
Xe^+	19.1	41.5	39.4	1.05
Kr^+	33.5	34.8	31.7	1.10
Ar^+	45.8	28.9	25.3	1.14
60-eV electrons	32.5	34.9	32.5	1.07
statistical	4.8	47.6	47.6	1.00
		Reaction II		
Xe^+	19.0	54.8	26.2	2.09
Kr^+	21.5	53.5	25.0	2.14
Ar^+	23.0	53.5	23.5	2.28
60-eV electrons	21.9	53.7	24.4	2.20
statistical	14.3	57.2	28.5	2.00

[a] Reaction I: $C_7H_5D_2^+(B^+) + C_6H_5CD_3 \rightarrow CD_3C_6H_4C(H,D)_2^+ + C_6(H,D)_6$. Reaction II: $C_7H_4D_3^+(B^+) + C_6H_5CD_3 \rightarrow CD_3C_6H_4C(H,D)_2^+ + C_6(H,D)_6$.

Table III. Relative Abundances of Product Ions Formed in Reactions 11-13

charge donor	IP	% distribution			$(C_8H_7D_2)CHD^+/(C_8H_7D_2)CH_2^+$
		reaction 11 $(C_8H_7D_2)CD_2^+$	reaction 12 $(C_8H_7D_2)CHD^+$	reaction 13 $(C_8H_7D_2)CH_2^+$	
COS^+	11.2	31.3	41.3	27.4	1.51
O_2^+	12.07	43.6	37.6	18.8	2.00
Xe^+	12.13	50.8	35.4	13.8	2.56
N_2O	12.9	50.4	34.5	15.1	2.28
CO_2^+	13.8	63.6	27.0	9.4	2.87
CO^+	14.0	64.8	26.2	8.9	2.94
Kr^+	14.0	63.0	27.0	10.0	2.70
N_2^+	15.6	37.4	38.6	24.2	1.60
Ar^+	15.8	28.0	41.6	30.4	1.37
60-eV electrons		51.0	33.4	15.6	2.14
statistical		4.8	47.6	47.6	1.0

variations of the abundances of the three $CH_3CD_2C_6H_4C(H,D)_2^+$ product ions as a function of the internal energy of $C_7H_5D_2^+(B^+)$ are given in Figure 3 and Table III. The product ion distribution obtained by electron impact (60 eV) is compared with the charge-transfer experiments in Table III, which also includes the product ion distribution to be expected for statistically scrambled $C_7H_5D_2^+$ (B^+) ions.

Experiments using $C_6D_5CH_2CH_3$ rather than $C_6H_5CD_2CH_3$ led to internally consistent product ion distributions, indicating no pronounced isotope effects on the H–D scrambling of $C_7D_5H_2^+$ as compared to $C_7H_5D_2^+$.

With the exception of the experiments involving Ar/$CH_3CD_2C_6H_5$ and $N_2/CH_3CD_2C_6H_5$, the ratio of the relative abundances of the $C(H,D)_2$ insertion product ions was invariant with reaction time up to 0.5 s (or ~500 collisions). In the Ar^+ and N_2^+-induced fragmentation of (ethyl-α,α-d_2)benzene, the relative contributions of reactions 13 and 12 showed an increase

$$C_6H_5CD_2^+ + C_6H_5CD_2CH_3 \rightarrow CH_3CD_2C_6H_4CD_2^+ + C_6H_6 \quad (11)$$

$$C_6H_4DCHD^+ + C_6H_5CD_2CH_3 \rightarrow CH_3CD_2C_6H_4CHD^+ + C_6H_5D \quad (12)$$

$$C_6H_3D_2CH_2^+ + C_6H_5CD_2CH_3 \rightarrow CH_3CD_2C_6H_4CH_2^+ + C_6H_4D_2 \quad (13)$$

over 11 as a function of reaction time until all $C_7H_5D_2^+(B^+)$ had reacted. The distribution represented in Figure 3 is that obtained after the reaction was completed.

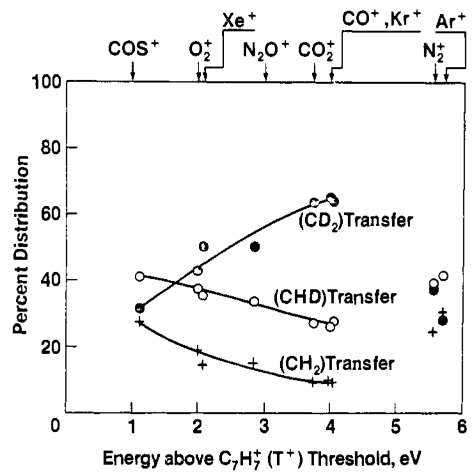

Figure 3. Relative abundances of $C_9(H,D)_{11}^+$ product ions formed in reactions of $C_7H_5D_2^+(B^+)$ ions with ethylbenzene, $CH_3CD_2C_6H_5$, plotted as a function of the energy above onset for tropylium (T^+) ion formation imparted to the parent ethylbenzene ion by charge transfer from the indicated charge donors. The product ions are $(C_8H_7D_2)CD_2^+$ formed in CD_2 transfer reaction 11 (●); $(C_8H_7D_2)CHD^+$ formed in CHD transfer reaction 12 (○); $(C_8H_7D_2)CH_2^+$ formed in CH_2 transfer reaction 13 (X).

Discussion

As originally suggested by Meyerson and collaborators,[17] it is now well established that the fragmentation of toluene and other substituted benzenes to give $C_7H_7^+$ results in the formation of the cyclic seven-membered ring T^+ structure[18] at the threshold for $C_7H_7^+$ ion formation.

In accord with the results reported in previous investigations,[1,2,4] both the charge-transfer (Figure 2) and the electron-impact (Figure 1) experiments show an initial increase in the population of benzyl ions with increase in internal energy of the $C_7H_8^+$ ion in toluene starting at the threshold. Figure 2 shows that in the

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(17) Grubb, H. M.; Meyerson, S. "Mass Spectrometry of Organic Ions"; McLafferty, F. W., Ed.; Academic Press: New York, 1963; p 453.

(18) Stapleton, B. J.; Bowen, R. D.; Williams, D. H., *J. Chem. Soc., Perkin Trans. 2* **1979**, 1219.

case of toluene there is reasonably good agreement between the energy dependence of the probability for B^+ and T^+ formation derived from the photodissociation data of Dunbar[1] and the results obtained in this study from charge-transfer experiments. In the photodissociation study, the internal energy of the parent ion is determined by the photon energy:

$$C_7H_8^+ + h\nu \rightarrow C_7H_8^{+*} + e^- \rightarrow C_7H_7^+ + H \quad (14)$$

while in the charge-transfer experiments:

$$C_7H_8 + M^+ \rightarrow C_7H_8^{+*} + M \rightarrow C_7H_7^+ + H + M \quad (15)$$

it can be assumed that the internal energy of the parent ion is given by the recombination energy of the charge donor. This is especially true when rare gas atomic ions are involved. It is conceivable that in the case of di- and triatomic ions, some of the internal energy is carried away as vibronic energy of the neutral, M. However, in view of the fact that when the charge donor CO^+ (recombination energy, 14.0 eV) is replaced by Kr^+ (recombination energy, 14.0 eV), there is, within experimental error, no change in the relative abundances of the B^+ and T^+ populations, or on the degree of deuterium scrambling in the benzyl ions produced from (ethyl-α,α-d_2)benzene (Table III), this effect may be minor. However, there are slight differences between results observed when O_2^+ (recombination energy, 12.1 eV) is replaced by Xe^+ (recombination energy, 12.1 eV), or when N_2^+ (recombination energy, 15.6 eV) is replaced by Ar^+ (recombination energy, 15.8 eV), which indicate that some energy is carried away as vibrational energy in the diatomic species (Table III).

In processes 11 and 12, the H atom product can only accept translational energy (the first electronic state is at 10.2 eV), so most of the excess energy will be stored as vibronic energy of $C_7H_7^+$. In the charge-transfer-induced fragmentation of ethylbenzene:

$$M^+ + C_6H_5CH_2CH_3 \rightarrow M + C_7H_7^+ + CH_3 \quad (16)$$

the CH_3 radical may take up as vibrational energy some of the excess energy imparted to the parent ion in the charge-transfer process. In this study we will assume as a first approximation that the bulk of the energy is stored as internal energy of the $C_7H_7^+$ fragment and that little energy is carried away as kinetic energy of the fragments. (At least for high kinetic energy charge donors, this approximation is correct.[19])

Because the $C_7H_7^+$ ion, be it B^+ or T^+, can dissociate (see eq 17) only when the internal energy exceeds ~4 eV,[20] at energies

$$C_7H_7^{+*} \rightarrow C_5H_5^+ + C_2H_2 \quad (17)$$

lower than this, possibly the only unimolecular reaction channel would be the proposed $B^+ \rightleftarrows T^+$ equilibrium (Scheme I). We shall now examine the structures and degrees of hydrogen scrambling to be found in $C_7(H,D)_7^+$ ions from ethylbenzene, toluene, and norbornadiene as a function of internal energy of the $C_7(H,D)_7^+$ ions.

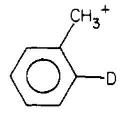
Ethylbenzene. The mechanism of formation of $C_7H_7^+$ from ethylbenzene is rather straightforward in that D-labeling electron-impact experiments show that the methyl group is eliminated intact.[16,21] In the present study (see Results), we find that the charge-transfer-induced fragmentation of (ethyl-α,α-d_2)benzene can be written as follows, even when $CH_3CD_2C_6H_5^+$ is formed with considerable excess internal energy:

$$M^+ + CH_3CD_2C_6H_5 \rightarrow CH_3CD_2C_6H_5^{+*} + M \rightarrow C_7H_5D_2^+ + CH_3 + M \quad (18)$$

A recent kinetic energy release study by Stapleton et al.[18] led to the conclusion that at low energies, ring expansion and contraction can occur prior to decomposition, apparently without involving the hydrogen atoms on the methyl group. In the present study, the occurrence of ring expansion in the parent ion is clearly evidenced by the observation that the benzyl-d_2 ions formed in process 17 transfer CHD and CH_2 in addition to CD_2 to (ethyl-α,α-d_2)benzene. In view of the fact that the CD_2F^+–C_6H_6 experiments (see Results) show that there is negligible H–D scrambling in the $C_6H_5CD_2^+$ ion prior to or during the methylene transfer reaction with an aromatic molecule, the observed product ions (Figure 3 and Table III) can be attributed to reactions 11–13 of $C_7H_5D_2^+$ with ethylbenzene.

If there were complete H–D scrambling in the benzyl-d_2 ions, the relative importance of reactions 11–13 would be 0.1:1.0:1.0. The data plotted in Figure 3 (and given in Table III) demonstrate that at all energies reaction 11 is of much greater importance than the 5% predicted from a statistical H-D-scrambling model. Also, there is a sharp increase in the importance of reaction 11 with energy, reaching 65% of the methylene transfer reaction around 4 eV above the onset for $C_7H_5D_2^+$ formation. It follows that, even when the benzyl ion has up to 3–4 eV in internal energy, hydrogen scrambling apparently is of minor importance. The rise in the population of $C_6H_5CD_2^+$ ions with energy can be rationalized if all the scrambling occurs in the *parent* ion prior to decomposition (involving a six–seven-membered ring expansion–contraction mechanism analogous to Scheme I), and as the energy is increased, the probability for loss of a CH_3 group prior to the occurrence of the scrambling mechanism increases.

If those $C_7H_5D_2^+$ ions which do not have two D atoms on the methylene group are produced in a process which involves complete H–D scrambling, one would predict a ratio of 1:1 for $C_6H_4DCHD^+$:$C_6H_3D_2CH_2^+$. As will be discussed later, this is the observed ratio for $C_7H_5D_2^+$ ions generated from toluene-α,α,α-d_3. In contrast, in $CH_3CD_2C_6H_5$, the ratio observed for $(C_8H_7D_2)$ CHD^+:$(C_8H_7D_2)CH_2^+$ is always greater than 1 and increases sharply from 1.5 to 2.9 with an increase in the internal energy content of the parent ion (Table III). These results indicate that methylcycloheptatriene ions which revert back to the ethylbenzene structure have a greater than statistical probability to retain a D atom in the α position:



$$\rightarrow C_6H_4DCHDCH_3^+ \rightarrow C_6H_4DCHD^+ + CH_3 \quad (19)$$

(where the cycloheptatriene ring in the initial reactant ion incorporates a D atom). The fact that the $C_6H_4DCHD^+$/$C_6H_3D_2CH_2^+$ ratio increases with energy is consistent with this interpretation in that the reduction in dissociative lifetime of the parent ion will reduce the number of passages over the energy barrier separating the six-membered from the seven-membered ring structure.

The rather abrupt fall in the abundance of the CD_2-transfer product ion (reaction 11) in the Ar^+- and N_2^+-induced fragmentation of (ethyl-α,α-d_2)benzene (Table III and Figure 3) indicates that extensive H–D scrambling may be occurring in the highly excited $C_7H_5D_2^+(B^+)$ ions. The appearance of a larger population of scrambled $C_7H_5D_2^+$ at higher energies is accompanied by an increase of T^+ population formed in the charge-transfer process 16. Both observations are consistent with the fast $B^+ \rightleftarrows T^+$ equilibration hypothesis put forward by McLafferty and

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(19) (a) Taubert, R. *Z. Naturforsch. A* **1962**, *19A*, 911. (b) Durup, J.; Heitz, L. *J. Chim. Phys. Phys.-Chim. Biol.* **1965**, *61*, 470. (c) Stanton, H. E.; Wexler, S. *J. Chem. Phys.* **1966**, *44*, 2959.

(20) Measurement of the appearance potential of $C_5H_5^+$ in a large number of aromatic compounds has led to a value of 12.3 ± 0.25 eV for the heat of formation of $C_5H_5^+$ (Tajima, S.; Tsuchiya, T. *Bull. Chem. Soc. Jpn* **1973**, *46*, 3291). A value of 11.06 eV has also been reported for the heat of formation of the cyclopentadienyl ion (Lossing, F. P.; Traeger, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1579), based on a measurement of the ionization potential of the cyclopentadienyl radical. When a value of 9.31 eV is taken for the heat of formation of B^+ (Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290. Rossi, M.; Golden, D. M. *Ibid.* **1979**, *101*, 1230), then the thermodynamic threshold for formation of $C_5H_5^+$ from B^+ is estimated to be 4.1 or 5.3 eV. When a value of 8.89 eV is taken for the heat of formation of T^+ (ref 11), the thermodynamic threshold for formation of $C_5H_5^+$ from T^+ is 4.5 or 5.8 eV. McCrery and Freiser (McCrery, D. A.; Freiser, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2903) observed a threshold for photodissociation of B^+ to give $C_5H_5^+$ as low as 3.55 ± 0.2 eV. This low-energy $C_5H_5^+$ may have the 1-vinylcycloprop-2-ene structure.

(21) Takamuku, S.; Sagi, N.; Nagaoka, K.; Sakurai, H. *J. Am. Chem. Soc.* **1972**, *94*, 6217.

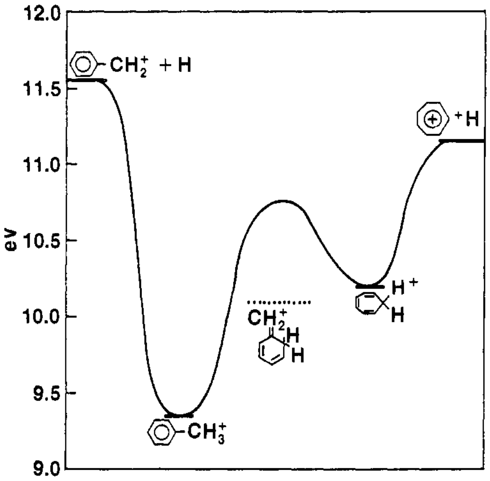

Figure 4. Potential surface cross section showing heats of formation of toluene and cycloheptatriene ions and the energies associated with dissociation to form the benzyl ion plus an H atom, or the tropylium ion plus an H atom. The barrier between the cycloheptatriene and the toluene ion is that calculated in ref 6. The heat of formation of the 5-methylene-1,3-cyclohexadiene ion (determined in ref 22) is also indicated; this ion has been suggested to be an intermediate in the $B^+ \rightleftarrows T^+$ isomerization process (ref 6).

Bockhoff,[4] although the energy at which it apparently occurs is substantially greater than the average internal energy (estimated) at which such processes are proposed to occur in the electron-impact ionization of toluene and cycloheptatriene and also higher than the calculated energy barrier for the $B^+ \rightleftarrows T^+$ isomerization.[6] In the present study, the randomization coincides approximately with the threshold for the formation of $C_5H_5^+$; in the Ar^+-induced fragmentation of ethylbenzene, about 20% of the $C_7H_7^+$ ions undergo this fragmentation.

Toluene. The rise of B^+/T^+ with increasing energy can be understood by considering the potential energy profile for interconversion and dissociation of the toluene and cycloheptatriene ions, depicted in Figure 4. A MINDO/3 calculation has indicated that 1.45 eV is required for the ring expansion of the toluene cation[6] and that the ring expansion occurs via a 5-methylene-1,3-cyclohexadiene ion intermediate. Recent experimental work[22] puts the heat of formation of the latter cation (9.97 ± 0.15 eV) between that of the toluene and cycloheptatriene cations and shows that at electron energies ranging from 14 to 30 eV, this parent ion has about an equal probability of forming $C_7H_7^+$ in the B^+ or the T^+ structure. Accepting[18] that ring expansion and contraction is not the rate-determining step in the H atom loss process, the gradual increase of the ratio B^+/T^+ at energies above the threshold for the formation of B^+ would be predicted from the energetics of the two competing fragmentation processes. At elevated energies, H atom loss from the parent $C_7H_8^+$ ion may also occur *without* prior rearrangement. This is indicated by the charge-transfer-induced fragmentation experiments with toluene-α,α,α-d_3. As shown in previous electron-impact and photodissociation studies,[23] the $C_7H_5D_2^+/C_7H_4D_3^+$ ratio increases with the internal energy content of the toluene ion (Table I). Actually, at the highest energy used in the study, the $C_7H_5D_2^+/C_7H_4D_3^+$ ratio exceeds the statistical value of 0.60 (Table I). As shown in Table II, the fraction of the $C_7H_5D_2^+(B^+)$ ions which transfer a CD_2 group to toluene in the reaction:

$$C_6H_5CD_2^+ + C_6H_5CD_3 \rightarrow CD_3C_6H_4CD_2^+ + C_6H_6 \quad (20)$$

increases from 19.1 to 45.8% over the energy range covered in this study. If the H(D) atoms in $C_7H_5D_2^+(B^+)$ were completely randomized, the probability of transferring CD_2 to toluene would be only 0.048.

The product ion distribution given in Table II also shows that the relative probability of occurrence of the other two reaction channels for $C_7H_5D_2^+(B^+)$:

$$C_6H_4DCHD^+ + CD_3C_6H_5 \rightarrow CD_3C_6H_4CHD^+ + C_6H_5D \quad (21)$$

$$C_6H_3D_2CH_2^+ + CD_3C_6H_5 \rightarrow CD_3C_6H_4CH_2^+ + C_6H_4D_2 \quad (22)$$

is close to unity, as predicted for completely scrambled $C_7H_5D_2^+$ ions. The $C_7H_4D_3^+$ ions, which must be produced mainly after the parent ion has made at least one passage over the isomerization barrier, lead to a $C(H,D)_2$-transfer product distribution, which is also close to the statistically expected one (Table II). The fact that the CHD/CH_2 transfer ratios for both $C_7H_5D_2^+$ and $C_7H_4D_3^+$ ions from toluene-α,α,α-d_3 are within a few percent of the statistically expected ratios (last column, Table II) demonstrates that, in contrast with the (ethyl-α,α-d_2)benzene case discussed above, H–D scrambling is essentially complete once ring expansion of the toluene ion has occurred. This implies that the ring expansion of the toluene-α,α,α-d_3 ion is not a simple single-step process where the two D atoms are retained in the 1,1-position of cycloheptatriene. Apparently, multiple passages must occur prior to the loss of the H(D) atom from toluene, or thermoneutral shuffling of H(D) atoms occurs in the cycloheptatriene ion. It follows that in contrast with results obtained in ethylbenzene, ring expansion and contraction in the toluene parent ion leads to the formation of $C_7H_4D_3^+(B^+)$ ions and a population of $C_7H_5D_2^+$ (B^+) ions that are essentially statistically scrambled. Therefore, the much higher than statistically predicted contribution of reaction 20 can clearly be ascribed to a direct cleavage of the C–D bond in a $C_6H_5CD_3^+$ ion that did not undergo a prior ring expansion:

$$C_6H_5CD_3^{+*} \rightarrow C_6H_5CD_2^+ + D \quad (23)$$

As in the case of ethylbenzene, the fact that direct cleavage without prior isomerization becomes more prevalent at higher energies is predictable on the basis of the shortening of the dissociation lifetime of the parent ion as a function of energy. With the assumption that the $C_6H_5CD_2^+$ ions formed in process 23 do not partake in the fast $B^+ \rightleftarrows T^+$ equilibrium suggested by McLafferty and Bockhoff,[4] the contribution of process 23 can be estimated by combining the information contained in Tables I and II; that is, process 23 accounts for 1.4, 6.4%, and 10.8% of all decomposition channels of the parent $C_6H_5CD_3^+$ ion at parent ion internal energies of 3.3, 5.2, and 6.9 eV, respectively. These energies are 1.1, 3.0, and 4.7 eV above the calculated appearance potential of the benzyl ion. The actual importance of process 23 is even higher if some of the B^+ ions isomerize to T^+ within $\sim 10^{-3}$ s (i.e., prior to the occurrence of the methylene transfer reaction 20).

Figure 2 shows a slight decline of the benzyl ion population from toluene at the highest energies covered in this work. Such a drop in the abundance of B^+ is also seen for $C_7H_4D_3^+$ ions from toluene-α,α,α-d_3 (Table I). As in the case of ethylbenzene, one can ascribe this increase of the T^+ population at high energies to a $T^+ \rightleftarrows B^+$ equilibrium, which takes over at high internal energies of the $C_7H_7^+$ ion. The fact that no high energy decrease of the B^+/T^+ ratio is observed for the $C_7H_5D_2^+$ ions (Table I) can be explained by the enhanced contribution of the direct C–D cleavage process 23, which leads to an enriched population of B^+ ions having a different (i.e., lower) probability for isomerization than the $C_7H_5D_2^+$ ions produced after ring expansion and contraction in the precursor parent ion. It can be surmised that at still higher energies, the abundance of the $C_7H_5D_2^+(B^+)$ ion population may decrease as it does in the case of ethylbenzene. Actually, if *all* $C_7(H,D)_7^+$ were to partake in a fast $B^+ \rightleftarrows T^+$ equilibrium, all three curves in Figure 2 should coincide at high energies. However, the ethylbenzene data (Table III) show that even at energies as high as 5.5 eV above the $C_7(H,D)_7^+$ threshold, H–D scrambling in the benzyl ions is still far from statistical. Attempts to increase the energy range of these experiments by including Ne^+ as a charge donor were unsuccessful in that the ionization cross section of Ne relative to that of the charge acceptor compound is too low to achieve a mixture composition in the ICR

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(22) Bartmess, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 335.

(23) (a) Howe, I.; McLafferty, F. W. *J. Am. Chem. Soc.* **1971**, *93*, 99. (b) Dunbar, R. A. *Ibid.* **1973**, *95*, 472.

for which charge transfer is the predominant mode of formation of $C_7(H,D)_7^+$. The problem is further aggravated by the fact that charge transfer from Ne^+ to the parent molecule leads predominantly to unstable $C_7(H,D)_7^+$ ions, which dissociate by loss of acetylene.

For the electron-impact ionization of toluene, the collisional activation study[4] shows a sharp drop-off in the B^+ population at electron energies above 15 eV (Figure 1), while the kinetic ICR study does not reveal such a reversal at electron energies up to 60 eV. This difference is unexplained. If the mean internal energy of the $C_7H_7^+$ formed at 60-eV electron energy is indeed around 2.8 eV,[4] no drop in the abundance of B^+ would be expected on the basis of the results of the charge-transfer experiments depicted in Figure 2. If one compares the product distribution resulting from the 60-eV electron-impact fragmentation of toluene-α,α,α-d_3 with that obtained in the charge exchange from Kr^+, a close correspondence is seen to exist. Because in the latter experiments, the $C_7(H,D)_7^+$ ions are formed with an excess energy close to 3 eV, one can conclude that the estimated internal energy[4] of 2.8 eV for T^+ formed with 60-eV electrons is a good approximation. The relative abundances of B^+ and T^+ ions observed when ionization is effected by electron impact in this study appears to be internally consistent with the relative abundances observed in the charge-transfer-induced dissociation experiments (Figures 1 and 2). As will be shown later, the same conclusion holds for norbornadiene, where a significant decrease of the B^+ population is actually observed at high electron energies (Figure 1).

Norbornadiene. Figure 2 shows the fraction of $C_7H_7^+$ ions observed to have the benzyl (B^+) structure, as a function of the excess energy above the threshold for formation of the tropylium ion (T^+) in norbornadiene. The energy dependence of the relative abundance of the benzyl ion observed in this compound is similar to the analogous results obtained in toluene (Figure 2). Note that because of the differences in appearance potentials, the energy imparted to $C_7H_7^+$ by charge transfer from any particular charge donor is 1.7 eV higher for norbornadiene as the precursor molecule than for toluene. Both curves show a relatively sharp rise in the relative abundance of B^+ in the low energy range and exhibit a maximum at about the same energy (3–4 eV). However, at any particular energy, norbornadiene shows a consistently lower B^+ population; the maximum in norbornadiene is 50%, as compared to 68% in toluene. The fact that the two curves do not exactly coincide may in part be due to differences in the potential surfaces governing the unimolecular reactions of the two parent ions. These differences are evidenced by the fact that the norbornadiene cation is the only $C_7H_8^+$ isomer which shows extensive C_2H_2 loss to yield a $C_5H_6^+$ fragment ion:

$$\text{norbornadiene}^+ \rightarrow C_5H_6^+ + C_2H_2 \qquad (24)$$

It has been demonstrated that this process occurs without appreciable carbon scrambling.[24] Also, in toluene it might be expected that the population of B^+ would be somewhat enhanced, since it is only in this molecule that B^+ ions can be formed directly by a C–H bond cleavage. As was shown in the last section, such a process accounts for at least 6% of the $C_7H_7^+$ ion formation in toluene at energies around 3 eV above threshold. Finally, we cannot rule out that in the case of norbornadiene, unreactive $C_7H_7^+$ ions other than tropylium ions are produced. All that can be said is that the $C_7H_7^+$ ions other than B^+ do not react with any of the major classes of of organic compounds (see Results). The collisional activation study of McLafferty and Winkler[5] indicates that $C_7H_7^+$ ions with a norbornadienyl structure are formed in addition to B^+. On the other hand, simple bond breakage in the norbornadiene cation would lead directly to an ipso-protonated benzyl radical, $C_6H_5(H^+)CH_2$, an ion in which a 1,2-proton shift would lead to the intermediate[6] proposed to account for the ring expansion of the toluene ion.

As in the other compounds, the falloff in the percent B^+ in norbornadiene at high energies is accompanied by extensive fragmentation to give $C_5H_5^+$, especially in the Ar^+ charge-transfer experiments, where the excess energy taken up by $C_7H_7^+$ reaches 6.7 eV. It is of particular interest that the falloff is also apparent in the electron-impact ionization of norbornadiene (Figure 1). The fact that this is not seen for toluene can be ascribed to a higher average internal energy of $C_7H_7^+$ formed in the electron-impact ionization of norbornadiene as compared to that of toluene. The appearance potential of $C_7H_7^+$ from norbornadiene is about 1.8 eV below that from toluene.

Structure of the $C_5H_5^+$ Ion. The $C_5H_5^+$ fragment ions exhibit two populations, one reactive and the other unreactive toward norbornadiene (see Results), indicating that there must be two distinct pathways leading to the production of two different $C_5H_5^+$ isomers. When Ar^+ replaces Kr^+ as the charge donor, the unreactive population increases from 19% to 50% of the observed $C_5H_5^+$. Because there is a corresponding decrease of the abundance of the $C_5H_6^+$ ion, the increase in the yield of the unreactive $C_5H_5^+$ ion can tentatively be ascribed to the dissociation process:

$$C_5H_6^+ \rightarrow C_5H_5^+ + H \qquad (25)$$

The reactive $C_5H_5^+$ ions which are produced in norbornadiene and which account for more than 90% of the total $C_5H_5^+$ population in aromatic compounds (see Results) may correspond to a higher energy linear structure (such as 3-penten-1-yne[19,25]) produced in reaction 17.

Conclusions

The present study shows that through an examination of the bimolecular kinetics (reaction rates and reaction modes) of ions one can obtain a detailed picture of the relative abundances of populations of different structural isomers. In addition, the results show that certain chemical reactions observed with deuterium-labeled reactant species are ideal for elucidating details of isomerization mechanisms. It is shown here that the reactions of the deuterium-labeled benzyl ion, $C_7(H,D)_7^+$, with toluene or with ethylbenzene are particularly well suited for analyzing the history of reactant benzyl ions (particularly since it can be shown that H–D scrambling does not occur in the ion–molecule complexes associated with these reactions). It has also been demonstrated here that parent molecule ions can be produced with internal energy contents that are well-defined (especially as compared to ions formed through electron impact) through charge transfer from thermal atomic or diatomic ions. It is evident from the isotopic labeling results that such charge-transfer reactions lead to the deposition of essentially all of the recombination energy of the charge donor in the product hydrocarbon ion.

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Registry No. Ethylbenzene, 100-41-4; toluene, 108-88-3; norbornadiene, 121-46-0; benzyl ion, 6711-19-9; tropylium ion, 26811-28-9.

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[24] Davidson, R. A.; Skell, P. A. *J. Am. Chem. Soc.* **1973**, *95*, 6843.

[25] Occolowitz, J. L.; White, G. L. *Aust. J. Chem.* **1968**, *21*, 997.