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THE STRUCTURE OF THE MOLECULAR ION OF C_7H_8 ISOMERS: AN ICR STUDY

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The structure of the molecular ion of C_7H_8 isomers and the $C_7H_7^+$ ion which it forms upon decomposition induced by electron impact has been the subject of numerous mass spectral studies.[1,2] Extensive d-labeling experiments,[3] for example, indicate that toluene undergoes a ring expansion to form the symmetrical tropylium ion either before or concommitant with the expulsion of the hydrogen atom. Carbon-13 labeling studies on the decomposition of the $C_7H_7^+$ ion[4,5] indicate that skeletal scrambling is also present within the system in addition to hydrogen scrambling.

Although no direct evidence for the structure of the non-decomposing molecular ion (of toluene) may be obtained from conventional mass spectral studies, various proposals have appeared in the literature. Meyerson[2] concluded that toluene rearranges to a cycloheptatriene-like structure of even higher symmetry, while Harrison[6] postulated an irreversible isomerization of the molecular ion to cycloheptatriene (transfer of an α-hydrogen to the adjacent ring carbon atom, followed by insertion of the methylene group at random between any two ring carbon atoms). More recently, Howe and McLafferty[7] in examining the degree of scrambling and variation of isotope effect with internal energy for cycloheptatriene and toluene have supported Harrison's postulation.

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On the other hand ion cyclotron resonance spectrometry[8] has proved useful in exploring differences in structure[9] through ion-molecule reactions. We present here preliminary studies of the reactivities of various $C_7H_8^{+\cdot}$ molecular ions towards abstraction of NO_2.

The evidence is that toluene retains its structural integrity and that no rearrangement, at least to cycloheptatriene or norbornadiene, takes place within the molecular ion in its reactions with methyl, ethyl, or isopropyl nitrate.

Selected ions from the ion-molecule reactions of alkyl nitrates have been shown to be potent electrophiles[10,11] in the low pressure ($\sim 10^{-5}$ torr) nitration of benzene and many organic functional groups at moderate electron energies (20 - 30 eV). Toluene not only undergoes an aromatic electrophilic addition reaction,[12] as confirmed by double resonance techniques,[13] but it also forms the same nitrated ion (*m/e* 138) by attack of the molecular ion, $C_7H_8^{+\cdot}$, upon the neutral alkyl nitrate (eq 1).

$$C_6H_5CH_3^{+\cdot} + RONO_2 \rightarrow CH_3C_6H_5NO_2^{+} + RO^{\cdot} \qquad (1)$$
$$R = CH_3,\ C_2H_5,\ (CH_3)_2C$$

Under similar conditions of pressure (C_7H_8 isomer ~ 0.2 μtorr; $RONO_2$ ~ 5.5 μtorr) and electron energy (30 eV), the molecular ions of cycloheptatriene and norbornadiene not only are unreactive towards the neutral alkyl nitrates, but the neutral C_7H_8 species are also inert to attack by alkyl nitrate ions. If any nitrated product is formed in the reaction of cycloheptatriene or norbornadiene, it is comparable in intensity to that of baseline noise, and at most, 1-2% of the intensity of the m/e 138 ion formed by the reaction of toluene.

We interpret these results--the lack of reactivity observed in the molecular ions of cycloheptatriene and norbornadiene, on the one hand, and the reactivity of the toluene molecular ion, on the other--as direct evidence that the toluene molecular ion and those of cycloheptatriene and norbornadiene are dissimilar; that is, the toluene molecular ion does not rearrange or convert to the cycloheptatriene structure before it reacts in an ion-molecule reaction.* Further, and quite importantly, because of the longer lifetime of ions required

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* Since ion-molecule reactions proceed without activation we feel that, in the absence of a suitable substrate, the ions which take part in the NO_2 abstraction would be "collected" in an ICR as the molecular ion. The possibility that the NO_2 abstraction is a collision-induced[14,15] (high energy) reaction is not ruled out, but even were that true, our observation that toluene and cycloheptatriene form structurally different molecular ions is even more remarkable.

for observation in ICR (ca. 10^{-2} sec) than in conventional mass spectrometry (ca. 10^{-5} sec), we believe that our findings must similarly hold true for these ions under conventional mass spectral conditions, that the non-decomposing $C_7H_8^+$ ions formed by toluene have not ring-expanded, and that ring-expansion to a cycloheptatriene-like ion must accompany the more energetic ions which then decompose.[16]

The discussion of the structure of the decomposing $C_7H_8^{+\cdot}$ ions and the $C_7H_7^+$ ions formed from these compounds will be included in a full paper, as this work is currently in progress.

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