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BENZYL IONS IN THE MASS SPECTRA OF FLUORO n-ALKYLBENZENES

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The question of benzyl _vs_ tropylium structures for ions of the general formula $XC_7H_6^+$ has received renewed attention recently in the electron impact mass spectra of nitrobenzyl compounds (1), bibenzyls (2), benzyl phenyl ethers (1,3,4), and _n_-butylbenzenes (5). Evidence for benzyl ion structures has been presented in those cases; whereas, the commonly accepted structure for $C_7H_7^+$ and related ions is a symmetrical (tropylium) ion (6). In studies on deuterium and C^{13}-labelled aromatics, considerable evidence has been marshalled in support of a symmetrical tropylium structure for $C_7H_7^+$ based upon its further decomposition to $C_5H_5^+$ (6,7,8). However, such information relates specifically only to the _decomposing_ $C_7H_7^+$ ions and does not necessarily bear directly on all $C_7H_7^+$ ions formed, the majority of which do not usually fragment further. On the other hand, the extensive hydrogen-deuterium scrambling in _α-d_$_3$-toluene and _ring-d_$_5$-toluene as shown in the nearly statistical loss of hydrogen and deuterium supports rearranged (symmetrical) parent ions which decompose to tropylium ion products (7). Further evidence for rearranged parent ion structures is found at threshold in measurements of appearance potential differences for $XC_7H_6^+$ from _meta_- and _para_- $XC_6H_4CH_2R$ (9).

We have applied the appearance potential differences method and assumptions[1] of Tait,

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[1] These assumptions include, reasonably, that the homolytic bond dissociation energies (leading to benzyl radicals) for the netural _m_- and _p_- isomers are approximately equal, that the heats of formation of these neutral isomers are also equal, and that the excess energies of ionization are also equal.

Shannon and Harrison (9) in order to determine the structures of ions formed at threshold from fluoro n-alkylbenzenes. Briefly, this difference method utilizes energy cycles for meta- and para- $FC_6H_4CH_2R$ leading to the equation below in which the difference in appearance potentials

$$A\,(\underline{m}\text{-}FC_7H_6^+) - A\,(\underline{p}\text{-}FC_7H_6^+) \approx I\,(\underline{m}\text{-}FC_6H_4CH_2\cdot) - I\,(\underline{p}\text{-}FC_6H_4CH_2\cdot)$$

for the $FC_7H_6^+$ isomers is approximately equal to the difference in ionization potentials of the same isomeric benzyl radicals ($FC_7H_6\cdot$). Thus, if the $FC_7H_6^+$ ions formed at threshold have benzyl structures with ring orientation of the substituent maintained, the difference in appearance potentials between meta and para isomers is expected to approximate the experimentally determined difference [0.40 eV] (10) between the ionization potentials of the corresponding benzyl radicals (9). If the difference in appearance potentials is found to be zero, we assume that rearrangement has occurred at threshold to structures (symmetrical tropylium) in which the original substituent orientation is no longer significant.

TABLE I

Appearance Potential Differences[a] for $FC_7H_6^+$ ions from meta and para Substituted $FC_6H_4CH_2R$

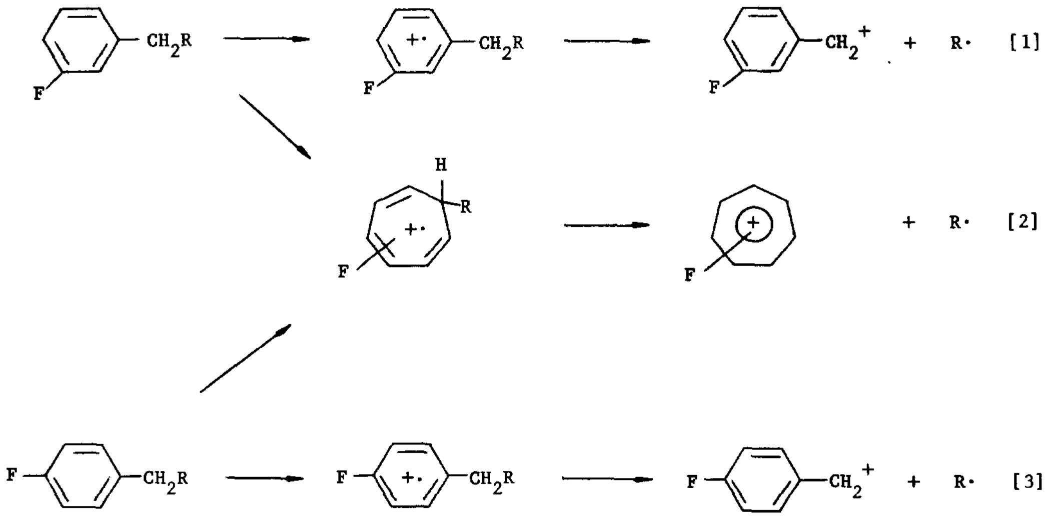
R	A(meta) - A(para)[b] (± 0.1 eV)	R	A(meta) - A(para)[b] (± 0.1 eV)
H	0.01	$(CH_2)_4CH_3$	0.45
CH_3	0.27	$(CH_2)_5CH_3$	0.02
CH_2CH_3	0.46	$(CH_2)_6CH_3$	-0.07
$(CH_2)_2CH_3$	0.50	$(CH_2)_8CH_3$	-0.19[c]
$(CH_2)_3CH_3$	0.40		

[a] Measurements were determined by the method of Warren using the unsubstituted n-alkylbenzene as internal reference and are an average of two or three determinations. J. M. Warren, Nature, 165, 810 (1950).

[b] The theoretical value calculated on the basis of benzyl ion formation from radical ionization potential data (see reference 10) is 0.40 eV.

[c] Ionization-efficiency curves had longer tails than the lower homologs and the error ascribed to the measurement is probably ± 0.2 eV.

The data shown in Table I clearly implicate benzyl ions at the threshold for the propyl, butyl, amyl and hexyl and possibly ethyl isomers and therefore suggest pathways [1] and [3] below. On the other hand, in agreement with earlier work (9), our data are consistent with a loss of the original substituent orientation (as shown by pathway [2]) in the fluorotoluene parent ions which produce $FC_7H_6^+$. It is particularly interesting to note that, based on the data of Table I, symmetrical (tropylium) ions reassert their presence in the mass spectra of fluoroalkylbenzenes with chains longer than hexyl. This departure in behavior was carefully checked by repetitive measurements on the fluorohexyl- and fluoroheptylbenzene isomers but is difficult to rationalize. If one is tempted to rationalize the toluene behavior in terms of the qualitative difference in leaving group (R = H vs alkyl), it is difficult to apply the same notion to explain the change from benzyl to tropylium structures in the longer alkyl chains. It is quite clear, however, from these data that a certain caution is needed in assuming tropylium ion structures apply whenever $C_7H_7^+$-like ions are formed, for benzyl ions frequently do intervene and the criteria for deciding when they do have not been fully established.



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