

Structural Characteristics of Non-decomposing $C_7H_7^+$ Ions from Some Methyl Ethers on Electron Impact

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Summary The structures of $C_7H_7^+$ ions formed from different precursors have been examined by means of a simplified form of the quasi-equilibrium theory.

from the molecular ions of cycloheptatrienyl methyl ether (I), methyl *p*-tolyl ether (II) and methyl benzyl ether (III)

With the exception of labelling experiments, which are often difficult and expensive, no method has produced a clear cut answer as to whether or not the formation of $C_7H_7^+$ ions in the mass spectra of aromatic compounds involves a ring expansion and, if so, the mechanism and timing of this.¹

We report an application of a simplified² form of the quasi-equilibrium theory (QET)³ to this problem. The application of more nearly exact forms of QET to the calculation of the complete mass spectra of molecules such as propane and toluene⁴ has been followed by the application of QET in approximation to various spectral features of more complex molecules at lower electron voltages.²

The simplification^{2†} used is similar to that of Williams,^{2a-e} except that the exponential term is held constant while a best fit is sought for the pre-exponential term, K_1 , in the

$$k(E) = K_1 \left[\frac{(E - E_1^0)}{E} \right]^{K_2} \quad (1)$$

crudely approximate form, equation (1).^{5,6} The errors expected from the approximation,^{2†} especially at low voltages, appear as a deviation in the "best-fit" values for the pre-exponential term from a constant value at low voltages. Previous investigators^{2b,e,f} have found that data may be fitted to this kind of equation, giving for simple cleavage reactions $K_1 \sim 10^{13} \text{ s}^{-1}$ (as expected for an uncoupled oscillator) and for reactions which proceed through rearrangement, under the same conditions K_1 values of 10^6 s^{-1} to 10^{10} s^{-1} .

A series of competing unimolecular decomposition reactions [(i) loss of H·, (ii) loss of Me·, (iii) loss of MeO·]

† It was initially assumed that both the $M - H\cdot$ and $M - Me\cdot$ reactions were simple cleavages, and so a value of K_2 was found (number of oscillators/7) such that K_1 for reactions (i) and (ii), taken as 9×10^{13} (C-H stretch) and 3×10^{13} (C-O stretch), fit the results.

‡ The generated partial spectra of toluene were examined as an external check to ensure that the results obtained for compounds (I), (II), and (III) were not fortuitous. It has been shown by labelling experiments that m/e 91 from toluene has ring expanded.

TABLE I

Ionization potentials and appearance potentials of compounds

	Methyl troyl ether	Methyl <i>p</i> -tolyl ether	Methyl benzyl ether	toluene
I.P.	7.23	7.83	8.76	8.78
A.P. $M - OMe\cdot$..	11.23	12.59	11.78	
A.P. $M - Me\cdot$..	10.26	11.77	11.47	
A.P. $M - H\cdot$..	10.72	11.91	10.75	12.31

* I.P. and A.P.'s were determined by a variation of the semi-logarithmic method.⁷

TABLE 2

"Frequency factors" for formation of the $C_7H_7^+$ ion from molecular ions at higher voltages

eV	Methyl troyl ether	Methyl <i>p</i> -tolyl ether	Methyl benzyl ether	Toluene
17	$0.9-1 \times 10^{14}$	$6-7 \times 10^{13}$	$2-3 \times 10^{14}$	3×10^8
18	$8-9 \times 10^{13}$	$5-6 \times 10^{13}$	$1-2 \times 10^{14}$	$2-3 \times 10^8$
19	$7-8 \times 10^{13}$	$4-5 \times 10^{13}$	$8-9 \times 10^{13}$	$1-2 \times 10^8$
20	6×10^{13}	$3-4 \times 10^{13}$	$5-6 \times 10^{13}$	$1-2 \times 10^8$

were studied at low voltage (up to 20 eV). Ionization potentials of these compounds and appearance potentials of the $M - H\cdot$, $M - Me\cdot$, and $M - OMe\cdot$ ions (Table I) were measured, and K_1 values for the formation of the $M - OMe\cdot$ ions ($C_7H_7^+$) were calculated.† The "best-fit" of the computer-generated K_1 terms for reaction (iii) with the actual intensity data for the formation of the m/e 91 ion is shown in Table 2, along with the data for the formation of m/e 91 ion from cycloheptatriene and toluene.‡

In all three cases, because K_1 for the $M - \text{OMe}\cdot$ reaction at the higher voltages (17–20 eV) is about 10^{13} , and therefore is roughly equivalent to the values assumed for the simple cleavages to give $(M - 1)$ and $(M - 15)$ ions, the m/e 91 ion (loss of $\text{Me}\cdot$ from the molecular ion) appears to result from a simple cleavage at the rate-determining step rather than from a rearrangement. Thus, the non-decomposing m/e 91 ions for these three systems maintain structural integrity: in the case of compounds (II) and (III), loss of methoxy is not concomitant with ring expansion;[§] the activated complex for this step cannot be related to that for scrambling of hydrogens.^{1k} Ions of m/e 91 from (II) and (III) which possess more energy than those

which do not decompose may ring-expand before they fragment further. Work is under way to extend this technique to the decomposition of these secondary ions (*i.e.* to determine whether the m/e 65 ions are produced from intact or ring-expanded decomposing m/e 91 ions) and to substituent effects on the decomposition of substituted aromatic compounds.

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[§] If one assumes that the $M - 1$ reaction is a rearrangement ($K = 1 \times 10^6$) rather than cleavage, the "frequency factor" for the $M - \text{OMe}\cdot$ reaction drops to 1×10^{13} , and must still be classified as a simple cleavage.

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