Rearrangement in the Molecular Ions of Halogenotoluenes prior to Fragmentation in the Mass Spectrometer

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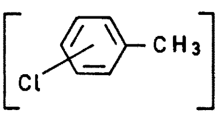
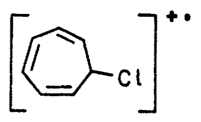
Summary The molecular ions of fluoro- and chlorotoluenes are shown to have undergone a ring-expansion rearrangement prior to fragmentation; in contrast, the bromo- and iodo-toluenes do not undergo such rearrangement prior to fragmentation.

IN the mass spectrometer, $C_7H_7^+$ ions generated from various different precursors (C_7H_7X) invariably lose C_2H_2.[1] These ions have been shown by deuterium[1] and carbon-13[2,3] labelling to have scrambled the hydrogen and carbon atoms prior to C_2H_2 expulsion.

We have compared the spectra of various fluoro-, chloro-, bromo-, and iodo-toluenes with the spectra of the corresponding benzyl halides and halogenobenzenes to obtain information concerning rearrangement (if any) in the molecular ions of these compounds prior to loss of the halogen radical. Ionisation and appearance potentials of various ions were also determined.

The mass spectra of 2-, 3-, and 4-chloro-toluenes are similar to one another; the molecular ion decomposes *via* loss of a hydrogen or, more favourably, a chlorine atom (Table 1). If no rearrangement occurs in the molecular ion prior to fragmentation, the loss of chlorine would involve a vinylic-type cleavage, similar to that in an unrearranged chlorobenzene ion-radical. A comparison (Table 1) with the partial spectrum of chlorobenzene shows that the loss of chlorine in chlorobenzene is much less extensive, relative to the molecular ion, than in the chlorotoluenes, suggesting a higher activation energy. This is confirmed by appearance potential measurements (Table 2); the activation energy for the loss of chlorine from the chlorotoluenes is *ca.* 0·8 ev less than that from chlorobenzene. It is highly unlikely that this difference is due entirely to a substituent effect of the methyl group on a vinylic cleavage. In contrast, the activation energy for the loss of chlorine from benzyl chloride where a benzylic bond is cleaved is only 1·4 ev. The data for the chlorotoluenes can be rationalised by postulating ring expansion of the molecular ions of the chlorotoluenes (I) to give chlorocycloheptatrienes (II).[4,5] Loss of the chlorine atom from (II), or from an ionised benzyl chloride structure formed by ring contraction from it, would then occur with a relatively low activation energy.


(I)


(II)

The difference in heats of formation of the cycloheptatriene and the toluene positive ion-radicals is 25 kcal/mole (240 — 215 kcal/mole; 1·1 ev),[6] and a similar difference between the ions (I) and (II) is assumed. Therefore, if the activation energy for loss of a chlorine radical from (II) (either directly, or after rearrangement to an ionized benzyl chloride structure) is less than *ca.* 1·7 ev [2·8 — 1·1 ev, the former figure being the mean energy to lose a chlorine radical starting with an ionized chlorotoluene (Table 2)], then *ca.* 2·8 ev represents the energy barrier which has to be surmounted to convert (I) into (II).

In contrast, the bromotoluenes give rise to mass spectra with $M^+ : M^+ - \text{Br}$ ratios similar to that for bromobenzene but very different from the ratios for benzyl bromide

TABLE 1

Intensities of M^+, $M^+ - X$ *and* $M^+ - H$ *ions in the* 70 ev *spectra of halogenobenzenes, halogenotoluenes, and benzyl halides*

	$[M^+] : [M^+ - X] : [M^+ - H]$			
X	F	Cl	Br	I
PhX	100 : 1 : 6	100 : 34 : 1	100 : 65 : 1	100 : 68 : 0
o-$MeC_6H_4.X$	100 : 2 : 170	100 : 162 : 26	100 : 70 : 7	100 : 71 : 0
m-$MeC_6H_4.X$	100 : 2 : 158	100 : 134 : 27	100 : 69 : 8	100 : 61 : 0
p-$MeC_6H_4.X$	100 : 2 : 162	100 : 185 : 43	100 : 71 : 15	100 : 45 : 0
$PhCH_2X$	100 : 6 : 167	100 : 323 : 17	100 : 775 : 3	100 : 5000 : 0

TABLE 2

Ionisation and appearance potentials (*in* ev) *of* M^+ *and* $M^+ - X$ *ions from halogeno-benzenes and -toluenes and benzyl halides*

X	Cl			Br			I		
	IP	AP	AP − IP	IP	AP	AP − IP	IP	AP	AP − IP
PhX	9·6	13·2	3·6	9·5	12·0	2·5	9·3	11·7	2·4
o-$MeC_6H_4.X$	9·0	11·8	2·8	8·8	11·2	2·4	8·9	11·3	2·4
m-$MeC_6H_4.X$	9·0	11·9	2·9	8·9	11·3	2·4	8·9	11·3	2·4
p-$MeC_6H_4.X$	9·0	11·7	2·7	8·9	11·4	2·5	8·9	11·3	2·4
$PhCH_2X$	9·2	10·6	1·4	8·9	9·1	0·2	8·8	9·2	0·4

(Table 1). The appearance-potential measurements (Table 2) show that the loss of bromine from the bromotoluenes most probably involves a vinylic cleavage as in bromobenzene, *i.e.* no ring expansion prior to fragmentation. The results for the iodotoluenes, when compared with the data of iodobenzene and benzyl iodide (Tables 1 and 2) follow the pattern found for the bromo-compounds; we conclude therefore that no ring expansion occurs.

It is emphasized that since an internal energy of *ca.* 2·4 ev is not sufficient to cause ring expansion in the bromotoluenes and iodotoluenes then, assuming only that the conversion of an ionized halogenotoluene into an ionized halogenocycloheptatriene requires an energy which is approximately independent of the halogen, our estimate of *ca.* 2·8 ev for this ring expansion seems reliable. This follows since the figure of 2·8 ev is dependent on the activation energy for chlorine loss from (II) being *less* than 1·7 ev; if it were equal to 1·7 ev, then the energy for ring expansion would be equal to or less than 2·8 ev. Since 2·4 ev does not cause ring expansion, the true figure for ring expansion must lie in the range 2·5—2·8 ev.

TABLE 3

Ionisation and appearance potentials (in ev) *of* M^+ *and* $M^+ - H$ *ions from fluorobenzene, fluorotoluenes, and benzyl fluoride*

	IP	AP ($M^+ - H$)	AP — IP
Ph	9·8	14·1	4·3
o-Me.C_6H_4.F	9·3	12·3	3·0
m-Me.C_6H_4.F	9·3	12·4	3·1
p-Me.C_6H_4.F	9·3	12·4	3·1
$PhCH_2F$	9·4	12·2	2·8

Hence it follows that if the energy required for fragmentation of the substituted toluene is greater than the energy required for rearrangement (ring expansion), then rearrangement occurs prior to fragmentation, and the spectra of the ring-substituted halogenotoluene would resemble that of the benzyl halide but not that of the halogenobenzene. The loss of hydrogen from fluorobenzene, fluorotoluenes, and benzyl fluoride are all high-energy processes (Tables 1 and 3); in the fluorotoluenes the activation energy for the loss of hydrogen is higher than the energy estimated for ring expansion (*ca.* 2·8 ev) and it is likely therefore that ring expansion occurs prior to loss of hydrogen (and fluorine) from the fluorotoluenes.

It is interesting to note from the appearance potential measurements (Table 4) that the activation energies for the production of the *m/e* 91 ion in toluene ($M^+ - H$) and *p*-xylene ($M^+ - CH_3$) are similar to that found for loss of chlorine from chlorotoluenes. This suggests that ring expansion occurs prior to loss of H and CH_3 from toluene and *p*-xylene respectively; this is indeed the case as shown by the scrambling of deuterium and hydrogens in the labelled compounds, prior to formation of the $C_7H_7^+$ ions.[7]

TABLE 4

Ionisation and appearance potentials (in ev) *of* M^+ *and* m/e 91 *ions from toluene, ethylbenzene, and* p-*xylene*

	IP (M^+)	AP (91)	AP — IP
Toluene	9·1	11·9	2·8
Ethylbenzene	9·0	11·3	2·3
p-Xylene	8·8	11·6	2·8

In contrast, the lower activation energy for the loss of CH_3 from ethylbenzene (2·3 ev) is consistent with absence of ring expansion; deuterium labelling showed no scrambling of the hydrogens in the β-position in the $M^+ - CH_3$ ion.[8]

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[7] Ref. 1, p. 496.

[8] Ref. 1, p. 488.