The Ion Kinetic Energy and Mass Spectra of the Isomeric Mono- and Di-chloronaphthalenes

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Summary The ion kinetic energy (IKE) and mass spectra of 1- and 2-chloronaphthalenes and seven dichloronaphthalenes have been recorded and the spectra of each set of isomers are strikingly similar; comparison of the daughter ion peaks obtained from the IKE spectra indicate chlorine randomisation over at least one of the rings in the mono-substituted compounds and over both rings in the isomeric dichloronaphthalenes.

THE mass spectra of many aromatic[1] and highly conjugated compounds[2] exhibit extensive H/D and carbon randomisation in the molecular ion prior to fragmentation. The mechanisms involved in the equilibration reactions are as yet unknown but clearly both carbon–carbon and carbon–hydrogen bond cleavages occur. It has also been shown that the halogen atom in the halogenotoluenes,[3] halogenobenzenes[4] lose positional identity upon electron impact; similarly the bicyclic halogenobiphenyls[5] and halogenodiphenylacetylenes[6] exhibit halogen (and H/D) randomisation in the molecular ion. It was therefore of interest to examine this effect in the bicyclic aromatic naphthalene nucleus.

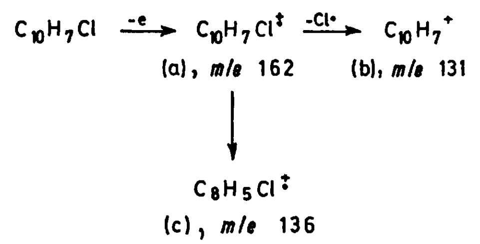
TABLE

IKE and primary ion mass spectra intensities of the halogenonaphthalenes[a]

Compound	M	$M-Cl$	$M-C_2H_2$	$M-Cl_2$	Relative IKE peak intensities 0·867E	0·821E	0·782E	[0·867E]/[0·821E]
1-Chloronaphthalene	100	20	<1					
2-Chloronaphthalene	100	18	<1					
Ia	100	11	<1	18	10·5	100	54	0·105
Ib	100	12	<1	20	10·5	100	54	0·105
Ic	100	14	<1	25	11·0	100	55	0·110
Id	100	11	<1	19	10·5	100	54	0·105
Ie	100	12	<1	21	10·0	100	55	0·100
If	100	14	<1	18	10·5	100	56	0·105
Ig	100	14	<1	19	10·0	100	54	0·100

[a] Recorded at 70 eV, 8 kV with a Dupont CEC-21-110B double focussing high resolution mass spectrometer.

The primary ion mass spectra of both 1- and 2-chloronaphthalene are similar (Table) and the fragmentation pattern, equation (1), shows loss of both Cl· and C_2H_2 from the molecular ion. The IKE[7] spectra of both compounds are identical (Figure 1) with daughter ion peaks at 0·840 and 0·785 E corresponding to the reactions (a) → (b) and (a) → (c) and the ratio of the two daughter ion peaks (*i.e.* [0·840 E peak]/[0·785 E peak]) was 0·13. These results indicate that their decomposing molecular ions in the first field-free region have similar energies and is evidence for



chlorine randomisation at least in the substituted ring of the naphthalene nucleus. Previously it was shown that in the deuteriated cyanonaphthalenes considerable, but not 100% H/D equilibration occurred in the molecular ion.[8]

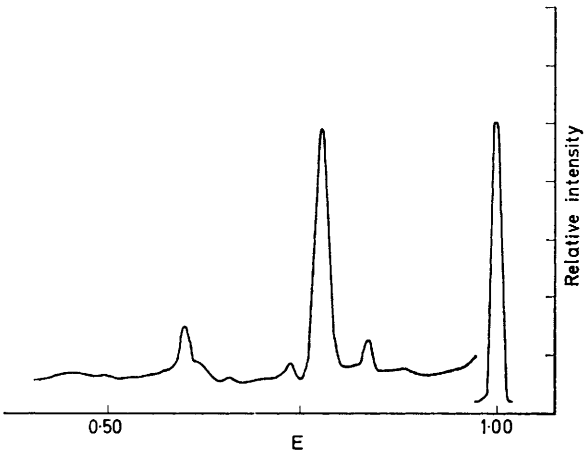
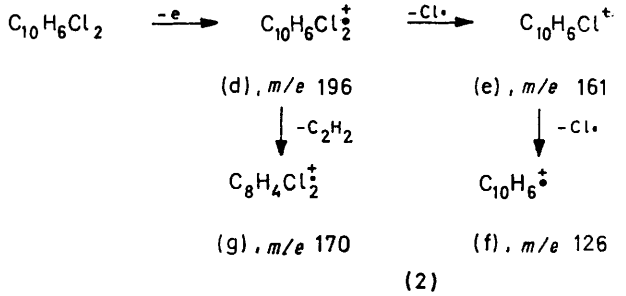
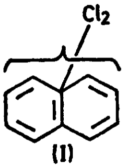


Figure 1. *IKE spectra of* 1-*chloronaphthalene*

The IKE and primary ion mass spectra of the dichloronaphthalene isomers (Ia—g) were also recorded to further examine the extent of chlorine equilibration. The fragmentation pattern is shown, equation (2), and confirmed by their respective IKE spectra (*e.g.* Figure 2) in which daughter ion peaks are observed at 0·867, 0·821 and 0·782 *E* corresponding to the reactions (d) → (g), (d) → (e) and (e) → (f). The relative peak intensities of both the IKE and primary ion spectra are similar for all the isomers (Ia—g) and the ratios, [0·867 *E*]/[0·821 *E*], obtained for the two daughter ion peaks which result from unimolecular decomposition of the molecular ion are also virtually indistinguishable. These data indicate that in the first field-free region of the mass spectrometer the decomposing molecular ions of all the dichloronaphthalenes have similar energies and energy distributions suggesting chlorine randomisation over all the carbon atoms of the naphthalene nucleus.



(2)



(I)

(a) 1·2, (b) 1·3, (c) 2·3
(d) 1·4, (e) 1·5, (f) 1·7, (g) 1·8

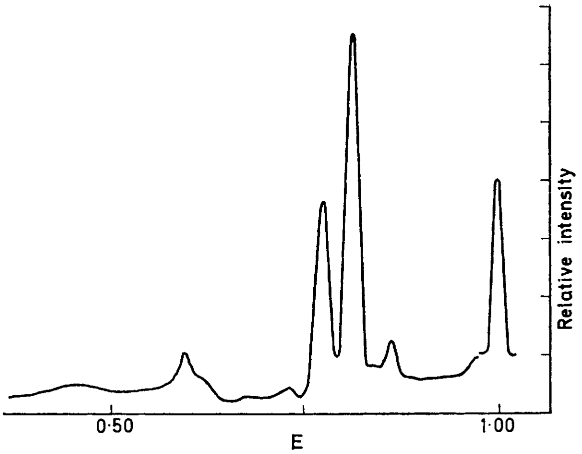


Figure 2. *IKE spectra of* 1,2-*dichloronaphthalene*

Beynon and his co-workers[9] have recently shown the advantages in studying H/D equilibration with IKE spectra and the present work illustrates a further useful application of this technique in demonstrating randomisation of chlorine in the isomeric chloronaphthalenes upon electron impact. The authors acknowledge the assistance of Dr. W. D. Jamieson.

(*Received*, 1*st December* 1971; *Com.* 2055.)

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