Studies on Hydantoin. Part 2.[1] Substituent Effects in 3-Arylhydantoins on the Formation of Aryl Isocyanate Ions using the Mass-analysed Ion Kinetic Energy–Direct Analysis of Daughter Ions

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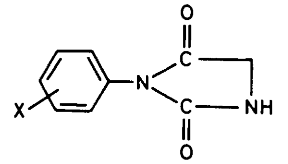
The unimolecular reaction of seven 3-arylhydantoins, relatively slow fragmentation in the free drift region, has been investigated by analysis of the mass-analysed ion kinetic energy (m.i.k.e.) spectrum using direct analysis of daughter ions (d.a.d.i.). Aryl isocyanate ion formation, which gives the base peaks or highly abundant ions, occurs through three pathways involving initial loss of CO, CH, and C_2H_2NO, respectively, and the substituent effects on the competing metastable transitions have been found. For electron-attracting groups in the *para*- or *meta*-positions, loss of CO· is the dominant process. The formation of the $M^{+\cdot} - C_2H_2NO^{\cdot}$ ions is the major pathway for electron-donating groups in the aromatic ring. The substituent effects on the formation of aryl isocyanates obey the Hammett equation. Correlation with σ and σ^+ are related semiquantitively to the solution chemistry of hydantoin.

The chemistry of organic ions produced from electron impact (e.i.) is related to their solution chemistry; there are many parallels between the behaviour observed for cations in the gas phase and that of organic solvent systems.[2] The potential usefulness of mass spectra in the unimolecular reactions of organic ions induced by electron impact is well established.[3] In recent papers, unimolecular dissociation of organic ions in the gas phase has been investigated by generating the ion in question in a conventional double-focusing mass spectrometer and considering the decompositions which occur during the metastable transitions.[4–6]

The 70 eV e.i. mass spectra of hydantoin (imidazolidine-2,4-dione),[7] thiohydantoins,[8–10] and 5-substituted hydantoins [7b,11,12] have been reported and discussed. Recently, the chemistry of 3-arylhydantoins (I) in solution has been studied,[13,14] but their mass spectra are less well known.[15] We report here the mass spectra of 3-arylhydantoin derivatives. Information about the chemistry of organic ions in a non-interactive environment may be acquired by investigating the mass-analysed ion kinetic energy (m.i.k.e.) spectrum of the molecular ion and the identified ions. The unimolecular reaction of hetereocyclic compounds has been of special interest.



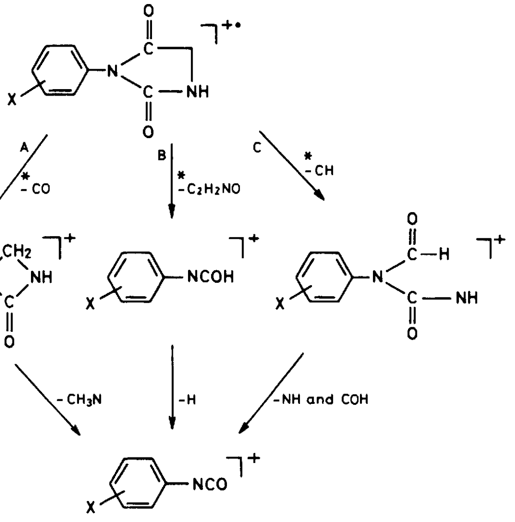
(I)

a; X = H
b; X = 4 - CH_3
c; X = 4 - CH_3O
d; X = 4 - Cl
e; X = 4 - NO_2
f; X = 3 - CH_3
g; X = 3 - Cl

Results and Discussion

In earlier papers [7,15] it was shown that cleavage of the hydantoin ring takes place by α-fission at the C=O group with loss of CO and RNCO. 3-Aryl groups are not eliminated before cleavage of the hydantoin ring. In this paper, we demonstrate by the direct analysis of daughter ions (d.a.d.i.) technique [16] that there are three pathways of aryl isocyanate ion formation, giving base peaks or highly abundant ions. Although the mass spectrum of 3-phenylimidazolidine-2,4-dione (Ia) has been previously reported and discussed,[15] these fragmentation pathways have not been detected.

The unimolecular reaction pathways of 3-arylhydantoins (Ia—g) have been determined with a double-focusing mass spectrometer with reversed Nier–Johson geometry.[16] The metastable transition spectra were recorded by automatic variation of the electrostatic analyser (e.s.a.) voltage from the initial value (E_0) downwards; each metastable peak arises from unimolecular decomposition in the free drift region of the reversed instrument and occurs at an e.s.a. voltage E which allows the assignment of parent (m_1) and daughter (m_2) mass numbers using the relationship $m_2 = m_1E/E_0$.



Scheme. Unimolecular reactions in the free drift region induced from molecular ions

The three patterns are observed in the free drift region from the molecular ions for (I) (Scheme) and their metastable transitions are reproduced in Figures 1 and 2.

The fragmentaion reaction of interest is formation of the $M^{+\cdot} - CH^{\cdot}$ ions (reaction C). These are only observed in the free drift region of the instrument because they are very unstable; they are not observed when the abundance of the molecular ion is decreased.

Measurements using the d.a.d.i. technique show that the

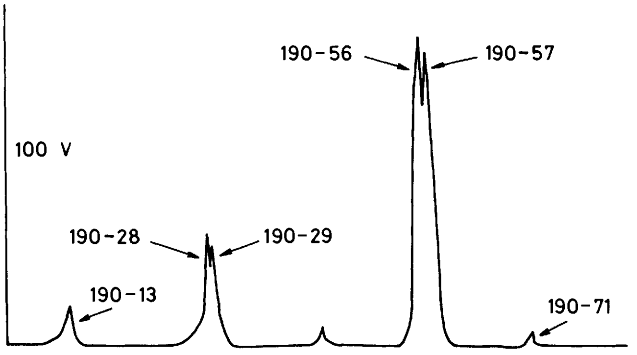


Figure 1. D.a.d.i. spectrum of the *m/e* 190 ion from 3-(3-tolyl)-hydantoin (If)

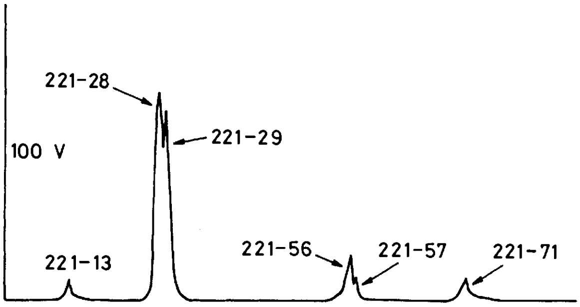
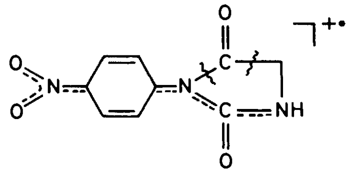
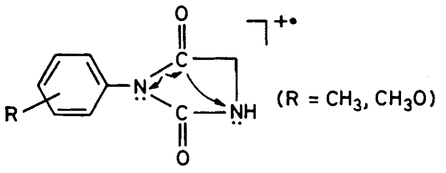


Figure 2. D.a.d.i. spectrum of the *m/e* 221 ion from 3-(4-nitrophenyl)hydantoin (Ie)





fragmentation pathway A carries over 50% of the total metastable transition current for *meta-* and *para*-electron-withdrawing groups; however, for (Ib, c, and f), the unimolecular reaction process B is dominant. These results demonstrate that aryl isocyanate ions are mostly produced from $M^{+\cdot} - CO$ or $M^{+\cdot} - C_2H_2NO$ ions, and that substituent effects affect the aryl isocyanate species produced.

The minor fragmentation pathway (reaction C) involves the loss of CH, NH, and CHO consecutively from the molecular ions to give aryl isocyanate ions in all the mass spectra of the 3-arylhydantoins (Ia—g), which are identified by the d.a.d.i. technique.

In the decomposition of iprodione [1-isopropylcarbamoyl-3-(3,5-dichlorophenyl)hydantoin], isopropyl isocyanate, and 3-(3,5-dichlorophenyl)hydantoin were formed. The aryl isocyanate is formed in the destruction of hydantoin.[17] For the 3-arylhydantoins, thermal dissociation is confirmed by the e.i. fragmentations.

Investigations of the alkaline hydrolysis of the hydantoins have shown that these compounds are converted into the corresponding hydantoic acids at various pH values.[13,18] The electrophilic reactivity of the 4-carbonyl group of the 3-arylhydantoins is worthy of notice since the delocalization of the non-bonding electrons of the nitrogen atoms does not extend to the carbonyl group, and the substituent effects in the aromatic ring have a direct effect on the group. This point is taken into consideration in the loss of the 4-CO group during unimolecular dissociation in a free environment. These effects should be sensitive to the nature of the rate-determining step,[13] since an electron-withdrawing group increases the electrophilic reactivity of the 4-carbonyl group. The m.i.k.e. spectra of the 3-arylhydantoins show these effects, and the results are in line with the solution chemistry. The molecular ions of the hydantoins (Ia—g) exhibit the same type of metastable transition spectra for the unimolecular fragmentations, *i.e.*, $M^{+\cdot} - CH^{\cdot}$, $M^{+\cdot} - CO^{\cdot}$, and $M^{+\cdot} - C_2H_2NO\cdot$, with various relative intensities for the substituents in the aromatic ring (Table 1).

In conclusion, the hydantoin ring is initially opened at the position α to 4-CO; in this process both the charge and the radical site are separated, and the loss of CO and C_2H_2NO exclusively from their molecular ions takes place competitively.

In general, the mass spectra of compounds (Ia—g) are characterized by the high relative abundance of the molecular ion peaks (Table 2).

Table 1. M.i.k.e. spectra of molecular ions from (Ia—g). The values are given as percentages of the total ion current

Compound	$M - CO$ and $M - CHO$	$M - C_2H_2NO$ and $M - C_2H_3NO$	$M - CH$
(Ia)	46 (148, 147)	36 (120, 119)	6 (153)
(Ib)	12 (162, 161)	73 (134, 133)	7 (177)
(Ic)	10 (178, 177)	71 (150, 149)	8 (193)
(Id)	51 (182, 181)	38 (154, 153)	4 (197)
(Ie)	68 (193, 192)	10 (165, 164)	5 (208)
(If)	14 (162, 161)	71 (134, 133)	6 (177)
(Ig)	511 (182, 181)	40 (150, 149)	5 (197)

The mass of the ion is given in parentheses. Intensities are reproducible to ±2%.

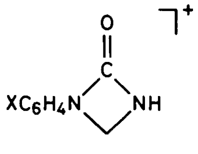
In aromatic systems the effect of substituents on mass spectra has been correlated by the Hammett equation.[19] The major fragmentation process indicated in the Scheme is the formation of aryl isocyanate ions. Examination of the spectra shows that the relative extent of this process (*i.e.* the relative abundance of aryl isocyanate ions in the various spectra) depends on the nature of the substituents. Theoretical aspects of this treatment have been discussed by McLafferty.[20]

For the case of 3-arylhydantoins, $Z = [XC_6H_4NCO^+]/[M^{+\cdot}]_X$ and $Z_0 = [C_6H_5NCO^+]/[M^{+\cdot}]_H$. This treatment may be adopted for *meta-* or *para*-monosubstituted hydantoins for correlations with both σ and σ^+ constants. The plot of log Z/Z_0 against σ and σ^+ shows an approximately linear correlation (Figures 3 and 4) and gives an inverse slope. Therefore cleavages undergone by 3-arylhydantoins on e.i. are related semiquantitatively to processes in solution.[13]

Experimental

Mass spectra were recorded on a Varian MAT 212 mass spectrometer with an electron beam energy of 70 eV and at a constant acceleration potential of 3 kV. Samples were introduced

Table 2. E.i. (70 eV) mass spectral data of 3-arylhydantoins (Ia—g)

	M^+		$XC_6H_4NCO^+$ (II)		 (III)		$XC_6H_4^+$ (IV)		$C_2H_2NO^+$ (V) (*m/e* 56)
Compd.	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	%
(Ia)	176	89.7	119	100	148	2.8	77	18.1	4.2
(Ib)	190	81.1	133	100	162	0.9	91	13.9	3.5
(Ic)	206	64.1	149	100	178	0.8	107	21.1	8.9
(Id)	210	81.3	153	100	182	0.6	111	6.8	5.0
(Ie)	221	100	164	48.8	193	2.1	123	2.7	16.2
(If)	190	100	133	88.3	162	1.6	91	11.6	8.3
(Ig)	210	85.1	153	100	182	4.3	111	7.4	19.9

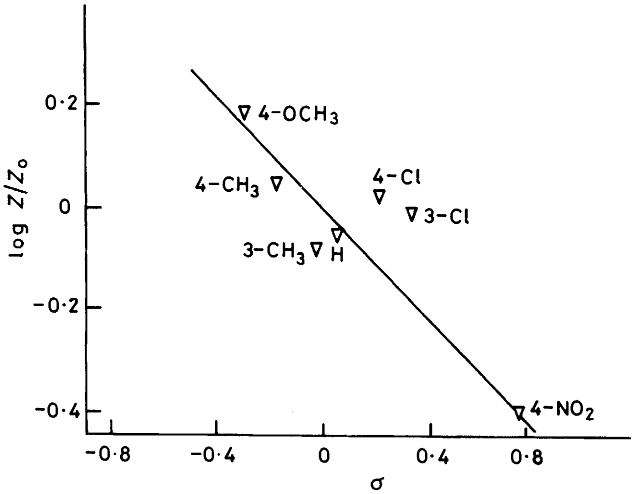


Figure 3. Relative intensities of $XC_6H_4NCO^+$ ions (II) from 3-arylhydantoins (Ia—g) plotted against σ values (ρ −2.1)

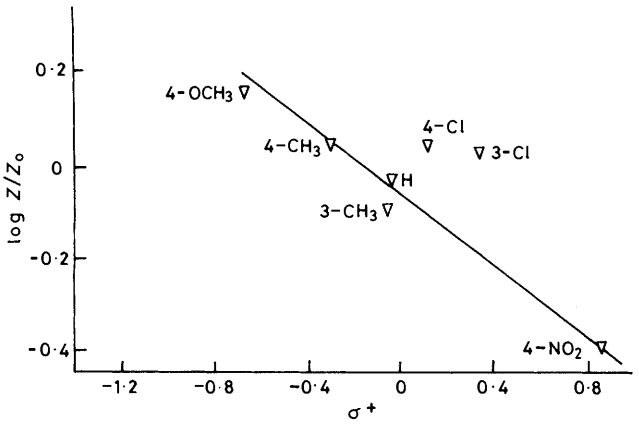


Figure 4. Relative intensities of the $XC_6H_4NCO^+$ ions (II) from 3-arylhydantoins (Ia—g) against σ^+ values (ρ −1.8)

via the direct inlet system with a cooled sample probe at a source temperature of 250 °C. Metastable transitions in the free drift region were normally observed at 3 kV and by varying the electrostatic analyser voltage by the d.a.d.i. technique.[16]

3-*Arylhydantoins*.—3-Phenylhydantoin was prepared by the reaction of the appropriate 2-chloroacetanilide with potassium cyanate in the presence of a phase-transfer catalyst (*e.g.* $Bu^n{}_4NCl$) in acetonitrile,[1] and recrystallized from water–ethanol, m.p. 155 °C (lit.,[21] 155 °C). Similarly prepared were (Ie), m.p. 255 °C (lit.,[22] 244 °C) and (Ig), m.p. 148 °C.

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