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Mass Spectrometry of Onium Compounds. XXIX.* Ionisation Potential in Structure Analysis of Valence Isomers

PER EGIL HANSEN and KJELL UNDHEIM

Department of Chemistry, University of Oslo, Oslo 3, Norway

The ionisation potentials of 1-substituted 1a,6a-dihydroindeno[1,2-*b*]azirin-6(1*H*)-one and 2-substituted isoquinolinium-4-oxide valence isomeric pairs show that thermal intermolecular isomerisation does not occur. The appearance potentials for the $[M-N_2]$ species from 3-substituted 3a,8a-dihydroindeno[1,2-*d*]triazol-8-(3*H*)-ones are in accordance with thermal formation of the corresponding indanoaziridines.

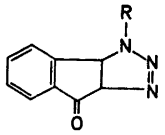
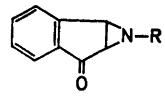
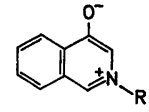
Simple pyridinium betaines are readily evaporated in the mass spectrometer.[2,3] The volatility could possibly be explained by isomerisation of the pyridinium-3-oxides to the corresponding non-charged 6-azabicyclo[3,1,0]hex-3-en-2-one. This electronic rearrangement is analogous to the reversible thermal valence isomerisation of phenyl substituted epoxides of cyclopentadienones and indenone to the corresponding pyrylium-3-oxide and the benzopyrylium-4-oxide.[4,5] We have therefore prepared some valence isomer pairs;[6,7] their mass spectral behaviour is discussed in this paper. The isomer pairs studied have incorporated a condensed benzene ring for stability reasons and thus consist of the indanones (II) and the isoquinolinium salts (III), in Table 1. The thermal bicyclic ring formation (III→II) or ring opening (II→III) is formally not permitted by the geometry of the system since the aziridine is constrained in a bicyclic structure of medium size (five-membered ring). During our work, however, it has been shown that closely related 6-imino- and 6-keto-1,1a,-6,6a-tetrahydroindeno[1,2-*b*]azirines could be reversible isomerised to isoquinolinium ylides.[8,9]

Structurally isomeric molecules may often have very similar mass spectra and cannot with certainty be differentiated by their fragmentation patterns alone. Energetically, however, the isomers may differ sufficiently for this to be detected in their ease of ionisation. We have on several occasions shown that measurements of ionisation potentials (IP) is a useful technique in structure analysis in the gas phase;[10–12] a recent paper reviews the use of IP and appearance potential (AP) in structure analysis.[13]

The IP's and AP's were arrived at by the semilog plot of the ionisation efficiency curves.[14] It is immediately apparent from a comparison of the IP data in Table 1 for the dihydroindeno-azirin-6-ones (II) and the isoquinolinium-4-oxides (III) that no thermal interconversion between the two series occurs in the mass spectrometer. Thus the IP's for the isoquinolinium betaines (about 7 eV) are at least 1 eV lower than the values for their aziridine isomers. It is further seen that the *N*-benzyl and *N*-phenyl isoquinolinium derivatives have very similar IP's which suggest that the primary ionisation is in the heterocycle. This suggestion is supported by the relatively weak influence of the phenyl *para* substituents on the ease of ionisation; *N*-phenylpyridinium-3-oxides have been found to behave similarly.[15] The phenyl aziridines can be considered as *N*,*N*-dialkylanilines in which case the variation in IP with the *para* substituent would show the expected pattern for ionisation in the phenyl ring.[16] Therefore the IP of *N*,*N*-dimethylaniline was measured and found to be 7.78 eV which agrees reasonably well with the value (8.13 eV) for the phenyl aziridine (IIa). Primary ionisation in the aromatic part of the indanone system would

* Part XXVIII, see Ref. 1.

Table 1. Ionisation potentials.

 (I)	AP[M−N_2]	 (II) IP	 (III) IP
(a) R=Ph	8.1±0.1	(a) 8.13±0.05 eV	(a) 7.10±0.05
(b) =*p*-MeOPh	7.8±0.1	(b) 7.68±0.05 »	(b) 6.93±0.05
(c) =*p*-NO_2Ph	8.8±0.1	(c) 8.71±0.05 »	(c) 7.29±0.05
(d) =CH_2Ph	8.1±0.1	(d) 8.15 [6]	(d) 7.10 [6]
(e) =Me	8.8±0.2		
(f) =Bu	7.8±0.2	(f) 7.90±0.1 eV	

appear to be excluded since the IP of indanone was found to be considerably higher (9.31 eV). No definite conclusion can be drawn, however, since the IP's of both the *N*-benzyl and *N*-butyl derivatives are also about 8 eV, and this can be interpreted in favour of initial ionisation on the aziridine nitrogen atom.

The *N*-phenyl aziridines (IIa−IIc) are formed in a heterogeneous mixture on pyrolysis of the corresponding 3a,8a-dihydroindeno[1,2-*d*]-triazol-8(3*H*)-ones (I); preparatively photolysis was superior.[7] In the mass spectra of the phenyl triazolines the highest mass number peak was that of a species having expelled two nitrogen atoms, in fact the mass spectrum was that of the corresponding aziridine (II). Dominating pyrolytic formation of aziridines was confirmed by measurements of the AP for the [M−N_2] species; the values showed good correlation with the IP values for the respective aziridines (II). Preparative pyrolysis of the benzyl derivative (Id), but not of the alkyl derivatives (Ie, If), yielded the respective aziridines. The mass spectra and the AP [M−N_2] for the benzyl derivative show aziridine formation as the principal pyrolytic pathway. The AP [M−N_2] for the butyl and methyl derivatives was variable and both spectra contained signals of *ca.* 1 % intensity corresponding to the molecular ion of the parent compound. As the alkyl aziridines were not available for comparison the butyl derivative (IIf) was separately synthesised by a Gabriel reaction from *trans*-2-bromo-3-butyl-*N*-aminoindan-1-one as described for the benzyl analogue (IId).[6] Both the IP value and its spectrum were similar to AP [M−N_2] for the triazoline (If) and its spectrum. As pointed out above, however, a weak molecular ion is present in its spectrum and a metastable for the [M−N_2] formation was seen by the defocusing technique. The closeness between the AP and IP values discussed indicates that pyrolysis is the major contributor to the [M−N_2] species. The AP

Table 2. Relative intensities of higher mass ions in the spectra.

(IIa)		(IIb)		(IIc)		(IIf)		(IIIa)		(IIIb)		(IIIc)	
m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
221	74	251	*100*	266	*100*	201	8	221	*100*	251	71	266	*100*
220	*100*	250	73	265	35	172	7	220	40	250	29	238	33
193	17	236	18	220	65	160	13	193	26	223	23	220	12
165	18	223	8	219	51	159	*100*	192	14	222	13	208	10
118	14	208	32	192	23	145	31	165	19	208	*100*	192	27
		118	20	118	17	131	58						
						118	14						

$[M-N_2]$ for the methyl derivative is significantly higher. Part of the increase may be due to the change from the butyl to the methyl group,[17] but it must be concluded that electron induced fragmentation of the evaporated parent molecule is here a major source for the species with mass number $[M-N_2]$. Comparisons of relative fragment intensities for the isomeric pairs in Table 2 show great similarities in the fragmentation patterns. Higher intensities for the [M−CO] fragments are generally found in the isoquinolinium series. The molecular ion is the base peak or a strong peak in all spectra except for the butylaziridine (IIf) where the base peak is formed by propylene expulsion (*m/e* 159) from the molecular ion. [M−H] appears more important for the aryl aziridines than for the isoquinolinium analogues, but this may be affected by the phenyl substituents. The fragmentation patterns are in general analogous to those briefly discussed for the benzyl pairs (IId/IIId) [6] and for the *N*-phenylpyridinium-3-oxides.[15] It suffices to point out that a characteristic signal for the indano-aziridines arises by expulsion of the whole NR-group to the species *m/e* 118; the mass number corresponds to that of indenone.

EXPERIMENTAL

The mass spectra and ionisation efficiency (i.e.) curves were recorded on an AEI-902 mass spectrometer as previously described.[14] The i.e. curves were interpreted by the semilog plot method.[18] The AP's and IP's are the average of three determinations.

Syntheses of the compounds have previously been described [6,7] with the exception of the butylaziridine (IIf).[19]

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