# MASS-SPECTROMETRIC INVESTIGATION OF ISATINS

## I. N-ALKYLISATINS

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UDC 543.51:547.756

It is shown that in the mass spectra of N-alkylisatins with a normal $C_1$-$C_{10}$ chain the intensity of the $[M - CO]^{+\cdot}$ and $[M - (2CO)]^{+\cdot}$ peaks characteristic for isatin and N-methylisatin decreases as the alkyl radical is lengthened, whereas the intensity of the peak formed as a result of successive loss by the molecular ion of a CO group and a portion of the radical as a result of cleavage of the bond at the $\alpha$-carbon atom increases. Fragments due to $\alpha, \beta, \gamma, \ldots$ cleavages, both without migration and with migration of the hydrogen atoms, appear in the spectra of N-alkylisatins commencing with chains containing more than two C atoms.

The mass spectra of isatin (I) and its N-methyl derivative (II) and their fragmentation schemes have been presented [1-3], but there are no data available on the dissociative ionization of compounds with a large number of carbon atoms attached to the nitrogen atom.

Our systematic comparative study of the mass spectrometric behavior of N-n-alkylisatins (A) showed that, despite the presence of a certain similarity between them and the mass spectra of isatins I-II, the character of fragmentation under the influence of electron impact is complicated to a considerable degree as the length of the alkyl chain increases.

As the alkyl chain becomes longer, the stability of the molecular ion $(W_M)$ [4] decreases from 0.21 to 0.07 with the regularity presented in Fig. 1 (curve 1). A minimum is observed for $C_6$-$C_7$.
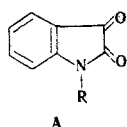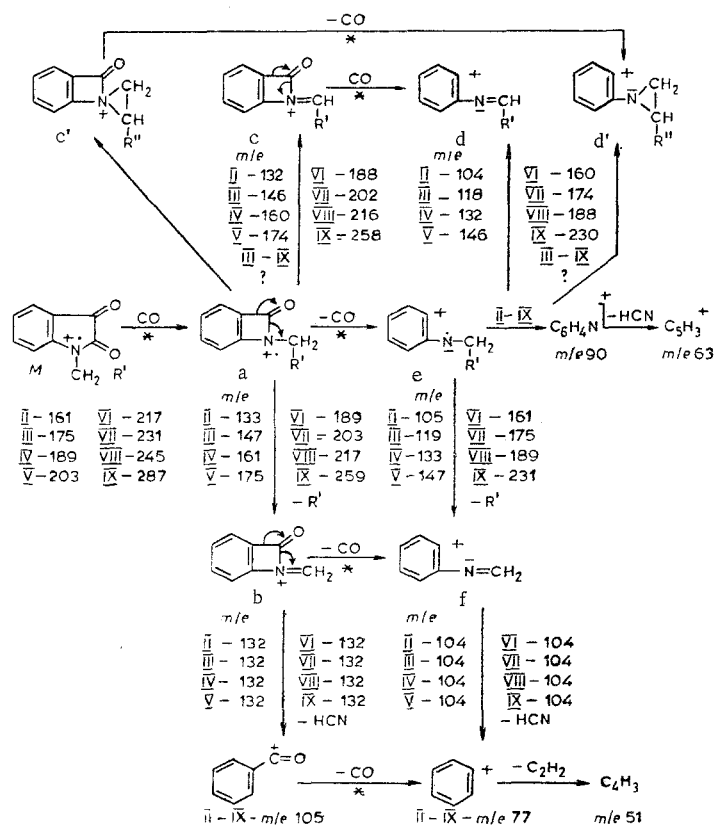


I R = H; II R = CH$_3$; III R = C$_2$H$_5$; IV R = C$_3$H$_7$;
V R = C$_4$H$_9$; VI R = C$_5$H$_{11}$; VII R = C$_6$H$_{13}$;
VIII R = C$_7$H$_{15}$; IX R = C$_{10}$H$_{21}$; X R = CD$_2$—CH$_3$

A

The presence of intense peaks corresponding to the successive elimination of two CO groups* from the molecular ion is characteristic for the fragmentation of I and II [2]. Our analysis of the mass spectra of I-IX enabled us to ascertain that, in addition to retention of some of the features specific for the mass spectra of isatins I and II, the character of the dissociative ionization depends on the length of the alkyl chain. The principal pathways of the fragmentation are presented in schemes 1 and 2 below.

As the length of the alkyl chain increases, the intensity of the $[M-28]^{+\cdot}$ peak, which, as already mentioned above, is characteristic for I and II, decreases sharply (scheme 1, M→$a$ transition). The character of the decrease, expressed in the form of a relationship between $I_{M-28}/I_M$ and the number of carbon atoms in the chain, is presented in Fig. 1 (curve 2).

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*The first CO group is ejected from the 2 position [3].

Scheme 1 (fragmentation):

−CO *

Structures: c', c, d, d' (top row)

Ion c (m/e):

| | | | |
|---|---|---|---|
| II − 132 | VI − 188 |
| III − 146 | VII − 202 |
| IV − 160 | VIII − 216 |
| V − 174 | IX − 258 |
| III − IX ? | |

Ion d (m/e):

| | |
|---|---|
| II − 104 | VI − 160 |
| III − 118 | VII − 174 |
| IV − 132 | VIII − 188 |
| V − 146 | IX − 230 |
| III − IX ? | |

Structures: M, a, e (middle row); −CO *

Isatin M:

| | |
|---|---|
| II − 161 | VI − 217 |
| III − 175 | VII − 231 |
| IV − 189 | VIII − 245 |
| V − 203 | IX − 287 |

Ion a (m/e):

| | |
|---|---|
| II − 133 | VI − 189 |
| III − 147 | VII − 203 |
| IV − 161 | VIII − 217 |
| V − 175 | IX − 259 |
| − R' | |

Ion e (m/e):

| | |
|---|---|
| II − 105 | VI − 161 |
| III − 119 | VII − 175 |
| IV − 133 | VIII − 189 |
| V − 147 | IX − 231 |
| − R' | |

$II-IX$ $C_6H_4N$ $m/e$ 90 $\xrightarrow{-HCN}$ $C_5H_3$ $m/e$ 63

Structures: b, f (lower row); −CO *

Ion b (m/e):

| | |
|---|---|
| II − 132 | VI − 132 |
| III − 132 | VII − 132 |
| IV − 132 | VIII − 132 |
| V − 132 | IX − 132 |
| − HCN | |

Ion f (m/e):

| | |
|---|---|
| II − 104 | VI − 104 |
| III − 104 | VII − 104 |
| IV − 104 | VIII − 104 |
| V − 104 | IX − 104 |
| − HCN | |

$\overset{+}{C}=O$ $\xrightarrow{-CO}{*}$ ... $\xrightarrow{-C_2H_2}$ $C_4H_3$

$II - IX$ − $m/e$ 105    $II - IX$ − $m/e$ 77    $m/e$ 51

Ion $a$ undergoes subsequent fragmentation via several pathways, of which the principal one is the formation of a fragment with m/e 132. The mechanism of its formation was established by recording the mass spectrum of N-1, 1-dideuteroethylisatin (X), in which a peak with m/e 134 instead of m/e 132 in the spectrum of III is recorded. This constitutes unambiguous proof that the $\alpha$- carbon atom bonded to the nitrogen atom is retained in its structure. Thus the formation of an ion with m/e 132 is realized as a result of $\beta$ cleavage of the C − C bond after elimination of a CO group (scheme 1, the M→$a$ →b transition). A characteristic feature of the mass spectra of isatins II-IX is a sharp increase in the intensity of the peak of ion b as the chain length increases from $C_1$ to $C_5$ with a subsequent more sloping decrease (curve 3). The fact that the point corresponding to the intensity of the peak of ion b for IV (curve 3) deviates by a value that is considerably greater than the methodical error is explained by the fact that in the case of isatin IV, two forms of ions with m/e 132, one of which, as seen in scheme 1, corresponds to ion b, the other of which corresponds to ion d, are formed. The increase in the intensity of the peak of ion b is due to the increasing stability of the ion, which increases as the stability of the radical undergoing detachment (R') increases.

One's attention is drawn to a peculiarity established during a study of the mass spectrum of N-1,1-dideuteroethylisatin X. The mass spectrum of nondeuterated III contains peaks with m/e 119 (52%) (e) and m/e 118 (39%) (d). In analogy with the fragmentation mechanism proposed for isatin II [2], ion d should have been formed as result of detachment of a hydrogen atom from the $\alpha$-carbon atom of ion e. In the case of an unambiguous mechanism of this sort and for isatin homologs one should have expected the appearance of peaks with m/e 121 (the analog of the peak with m/e 119) and m/e 119 (the analog of the peak with m/e 118) in the mass spectrum of X. However, the mass spectrum of X contains peaks with m/e 121 and 120 (instead of the expected peak with m/e 119), the intensity ratio of which is approximately the same as for the peaks with m/e 119 and 118 in the spectrum of isatin III. In addition, the mass spectrum of X contains peaks with m/e 149 (the analog of the peak with m/e 147, ion $a$) and m/e 148 (the analog of the peak with m/e 146, ion c). The established facts prove that detachment of a hydrogen atom from ions $a$ and e in the case of III occurs primarily from the $\beta$-carbon atom rather than from the $\alpha$-carbon atom with the formation of ions, the hypothetical structures of which are presented in scheme 1 (the $a$ →c' →d' and e →d' transitions). The subsequent disintegration of the ions described is presented in the same scheme.

The mass spectra of III-IX contain fragments with even-numbered m/e values, which are formed during cleavage of the N − C bond and $\alpha$, $\beta$,$\gamma$,... cleavages of the alkyl chain. Their intensity is low and decreases in the same order. Of particular interest are the peaks of ions with odd-numbered mass values,
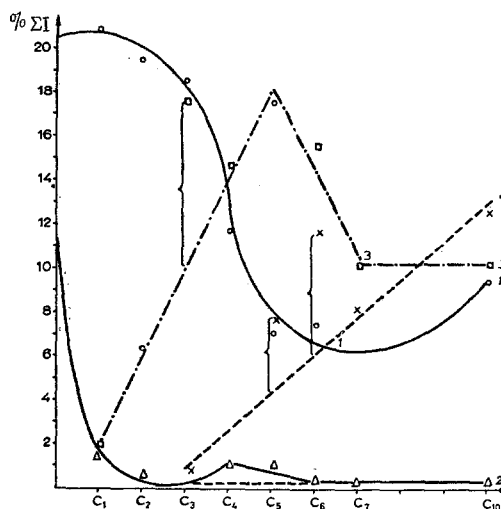
Fig. 1. Change in the fraction of the total ion current as a function of the length of the alkyl chain in the mass spectra of II-IX: 1) $W_M \cdot 100$; 2) $J_{M-28}/J_M$; 3) peak intensity at m/e 132; 4) peak intensity at m/e 161.

which arise as a result of the loss by the hydrocarbon radical of neutral fragments with migration of a hydrogen atom to the residual portion of the molecule. Part of these transitions are confirmed by meta-stable peaks. Their intensity increases as the length of the hydrocarbon chain increases (II →IX) (scheme 2). The most stable ion is the ion with m/e 161, the intensity of which in the mass spectrum of IX is 100%; thi ion is followed, in decreasing order, by ions with m/e 175, 189, 203, etc. The subsequent disintegration of these ions is realized via scheme 1, which is also confirmed by metastable transitions. The latter makes it possible to assume with a certain degree of confidence that their structure is analogous to the structure of the corresponding alkylisatins (scheme 2).

As we have already mentioned above, the most stable of the ions with odd-numbered masses is the ion with m/e 161; its intensity increases regularly as the length of the alkyl chain increases (curve 4). The
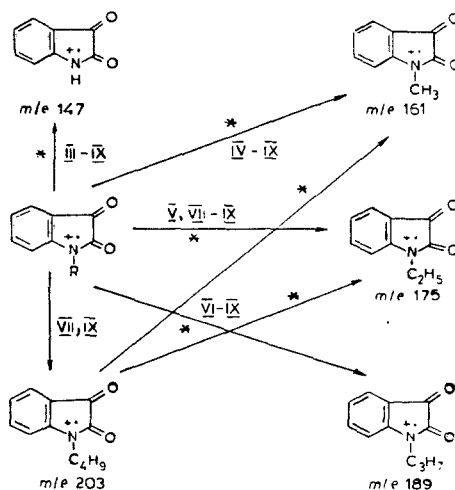


deviation to the larger side of the observed regularity for the points in the case of VI and VII is explained by the fact that the peak with m/e 161 is a composite peak due to contributions of $M - C_4H_8]^{+\cdot}$ and $[M - (2CO)]^{+\cdot}$ ions in the case of VI and $[M - C_5H_{10}]^{+\cdot}$ and $[M - (C_3H_6 + CO)]^{+\cdot}$ ions in the case of VII.

Thus it was established that two principal fragmentation pathways are realized in N-alkylisatins. The first pathway involves ejection of CO with subsequent cleavage of the alkyl chain at the $\alpha$-carbon atom, and the second pathway involves fragmentation of the hydrocarbon radical to give lower homologs of isatin, which in turn undergo disintegration in accordance with the regularity common to isatins.

Compounds II-IX were obtained by reaction of the sodium salt of isatin with the appropriate alkyl bromides [5]. The compounds were purified by column chromatography to remove the unchanged isatin and side products that fluoresce in UV light (elution by benzene). The starting 1,1-dideuteroethyl bromide was synthesized by the method in [6]. The individuality of the compounds was monitored by thin-layer chromatography on Silufol silica gel in benzene and benzene – acetone (1:1) systems.

The mass spectra were recorded with an MKh-1303 spectrometer equipped with a glass system for direct introduction of the sample into the ion source. The vaporization temperature was 90-120°, the ionization chamber temperature was 150°, the ionizing voltage was 70 eV, and the emission current was 1 mA. The reproducibility of the mass spectra during recording in the course of a day was 2-2.5 rel. %, as compared with 8-12 rel. % for recording over a longer period.

Mass spectra of isatins I-IX, m/e (relative intensity, %):

I — 147(82), 119(100), 92(57), 91(17), 90(6), 76(7), 75(3), 64(24), 63(17), 52(6), 50(9);

II — 161(100), 133(31), 132(9), 105(56), 104(70), 92(11), 90(9), 78(38), 77(19), 76(8), 64(11), 63(13), 51(11), 50(13);

III — 175(100), 147(8), 146(12), 132(32), 119(57), 118(38), 105(13), 104(37), 92(9), 91(12), 90(18), 78(13), 77(28), 76(9), 64(10), 63(10), 51(10), 50(9);

IV — 189(98), 161(3), 160(2), 147(4), 146(7), 133(28), 132(100), 119(17), 118(7), 105(12), 104(31), 92(6), 91(7), 90(14), 78(11), 77(32), 76(8), 64(6), 63(7), 51(12), 50(7);

V — 203(78), 175(19), 174(2), 161(22), 160(4), 147(17), 146(19), 133(22), 132(100), 119(73), 118(11), 106(12), 105(5), 104(12), 92(11), 91(8), 90(17), 78(7), 77(37), 76(8), 64(7), 63(8), 51(13), 50(7);

VI — 217(41), 189(7), 188(3), 174(3), 161(45), 160(7), 147(18), 146(20), 133(22), 132(100), 119(35), 118(9), 106(9), 105(15), 104(11), 90(16), 77(39), 76(8), 64(4), 63(6), 51(12), 50(6);

VII — 231(51), 203(2), 202(1), 189(2), 188(1), 175(18), 174(6), 161(75), 160(10), 147(24), 146(22), 133(21), 132(100), 119(30), 118(8), 106(11), 105(15), 104(12), 90(15), 77(37), 64(4), 63(4), 51(11), 50(2);

VIII — 245(58), 217(3), 216(2), 189(8), 188(5), 175(33), 174(12), 161(81), 160(13), 147(23), 146(24), 133(23), 132(100), 119(29), 118(10), 106(13), 105(18), 104(13), 77(39), 64(5), 63(5), 51(12), 50(6);

IX — 287(75), 259(4), 258(2), 231(1), 230(1), 216(2), 203(1,5), 202(5), 189(13), 188(11), 175(44), 174(17), 161(100), 160(11), 147(22), 146(19), 133(18), 132(80), 119(27), 118(7), 106(12), 105(14), 104(9), 77(27), 64(3), 63(3), 51(1), 50(5).

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