

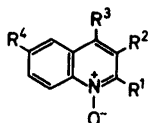
## Thermal Fragmentation of Quinoline and Isoquinoline N-Oxides in the Ion Source of a Mass Spectrometer

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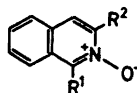
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The loss of an oxygen atom from the molecular ions of quinoline and isoquinoline *N*-oxides has been shown to be due to thermal, rather than electron impact fragmentation. This class of compound provide excellent test substances for determining the degree of thermal fragmentation accompanying the use of a direct inlet system attached to a mass spectrometer.

The appearance of an abundant *M*-16 ion was frequently observed<sup>1-8</sup> in the mass spectra of heteroaromatic *N*-oxides and this fragmentation was originally suggested to be diagnostic of this functionality.<sup>1</sup> Alkyl substitution adjacent to the *N*-oxide was found<sup>2,4,7</sup> to result in a more pronounced *M*-17 ion, presumably due to an *ortho* effect.<sup>9</sup> In contrast to these results we observed<sup>9</sup> only low intensity *M*-16 and *M*-17 ions in the mass spectra of a series of quinoline and isoquinoline *N*-oxides. We recently had occasion to repeat these mass spectra under instrumental conditions in which the ion source of the mass spectrometer was operated considerably hotter (180°C) than the 70°C previously utilized.<sup>9</sup> We found for instance that quinoline *N*-oxide-2-*d*<sub>1</sub> exhibited an *M*-16 ion of 100 % relative abundance as compared to the



- Ia: R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
 Ib: R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
 Ic: R<sup>1</sup> = R<sup>3</sup> = CH<sub>3</sub>; R<sup>2</sup> = R<sup>4</sup> = H  
 Id: R<sup>1</sup> = R<sup>2</sup> = R<sup>4</sup> = H; R<sup>3</sup> = CH<sub>3</sub>  
 Ie: R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H; R<sup>4</sup> = CH<sub>3</sub>  
 If: R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H  
 Ig: R<sup>1</sup> = C<sub>6</sub>H<sub>5</sub>; R<sup>3</sup> = R<sup>4</sup> = H; R<sup>2</sup> = CH<sub>3</sub>



- IIa: R<sup>1</sup> = R<sup>2</sup> = H  
 IIb: R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H  
 IIc: R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>

previously recorded<sup>9</sup> value of 4 % for the undeuterated compound. This result prompted us to redetermine, using the mass spectrometer ion source at 180°C, the spectra of the quinoline and isoquinoline *N*-oxides previously published<sup>9</sup> in order to gauge the extent of thermal fragmentation in this series of compounds.

Table 1. Effect of ion source temperature on the M-oxygen ion abundance in a series of quinoline and isoquinoline *N*-oxides.

Compound	M-oxygen/M <sup>+</sup>		
	A. E. I. MS-9 ion source 180°C	Finnigan 1015 ion source 180°C	Varian Atlas CH-4 ion source <sup>a</sup> 70°
Ia	0.84	3.71	0.04
Ib	0.87	2.58	0.04
Ic	1.37	3.90	0.11
Id	1.10	0.70	0.05
Ie	0.85	0.79	0.09
If	12.5	9.8	0.47
Ig	2.92	6.4	0.02
IIa	2.08	0.96	0.12
IIb	1.67	3.6	0.11
IIc	1.40	5.8	0.19

<sup>a</sup> Taken from previous measurements.<sup>9</sup>

Table 1 compares the values obtained for the ratio of the abundances of M-16/M<sup>+</sup> using two mass spectrometers (whose ion source temperatures were maintained at 180°C) with the values previously recorded<sup>9</sup> using an ion source temperature of 70°C. In all cases where a hot ion source was utilized the value of the ratio M-16/M<sup>+</sup> has dramatically increased as compared to the cool (70°C) ion source. It would seem that the abundance of the M-16 ion in all the quinoline and isoquinoline *N*-oxides examined with a 180°C ion source results from thermolytic fragmentation prior to electron impact. This pyrolysis phenomenon would explain the abundant M-16 ions recorded<sup>1-7</sup> by other investigators.\*

Without exception all the *N*-oxides examined, which lack a methyl group adjacent to nitrogen (Ia, Id, Ie, and IIa), displayed a metastable ion in their respective mass spectra for the process M-16 → M-17. This supports our previous contention (based on low eV spectra)<sup>9</sup> that the M-17 ion in these compounds results from the elimination of a hydrogen atom from the

\* The appearance of intense M-16 ions in the mass spectra of heteroaromatic compounds does not mitigate against the use of mass spectrometry for the identification of this class of compound. Clearly one should not attribute this ion's presence in a mass spectrum to electron impact phenomena.

M-16 species. Since thermal fragmentation is responsible for the high M-16 ion abundance in these compounds it is apparent that the M-17 ion yield will also be increased.

In the case of the compounds (Ib, Ic, IIb, and IIc) containing a methyl group adjacent to the N-oxide linkage, two distinct processes contribute to the M-17 ion yield. First direct loss of a hydroxyl radical from the molecular ion (due to the *ortho* effect), and secondly, loss of a hydrogen atom from the parent amine, obtained as a pyrolysis product in the ion source. Both these fragmentations are supported by metastable ion evidence in all cases examined by us. In those methyl substituted derivatives (Id and Ie) lacking a methyl group adjacent to the N-oxide group, the only discernable mode of formation (metastable ion observed) of the M-17 species is by elimination of a hydrogen radical from the parent amine.

The ion corresponding to the parent amine in all the N-oxides examined eliminates HCN as determined from recognition of the required metastable ions. This behaviour is in accord with the fragmentation processes of quinoline and isoquinoline bases<sup>10</sup> (the product from thermolytic deoxygenation of quinoline and isoquinoline N-oxides) which readily eliminate HCN from their molecular ions.

The true electron impact processes we described<sup>9</sup> for quinoline and isoquinoline N-oxides can be easily recognized in the mass spectra determined at 180°C where they are superimposed on the artefact ions resulting from pyrolysis of the N-oxide to the corresponding amine.

It is apparent that N-oxides of the quinoline and isoquinoline series provide superb reference compounds for ascertaining the degree of pyrolysis of a direct inlet system.

## EXPERIMENTAL

Mass spectra were recorded on A. E. I. MS-9 and on Finnigan 1015 Quadrupole mass spectrometers at 70 eV. In both instances the temperature of the ion source was maintained at 180°C and samples were introduced by the direct inlet system. The Finnigan 1015 Quadrupole mass spectrometer is connected to a data system which has been described.<sup>11</sup>

Compounds used in this investigation were of analytical purity and were prepared by published procedures.<sup>12</sup>

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