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Mass Spectra of Oxamides

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Mass spectra of oxamide, *N,N'*-dialkyl- and *N,N'*-diaryloxamides have been studied. Important fragmentation processes are cleavage of the C—C bond between the two carbonyl groups and hydrogen rearrangements reflecting the 1,2-dicarbonyl- and amide functionality, respectively. A specific loss of the *ortho* substituent from the molecular ions of aryl substituted oxamides is observed. Ortho effects resulting from interaction of the -NHCO moiety with a nitro or methoxy substituent are observed in the decomposition of some fragment ions.

In order to investigate the influence of the —NHCOCONH— grouping on the fragmentation pattern of oxamides, the mass spectra of oxamide and a series of *N,N'*-dialkyl- and *N,N'*-diaryloxamides are reported and discussed. Resemblance to the behaviour upon electron impact of both amides [1] and acyclic compounds with a 1,2-dicarbonyl arrangement [2,3] (α-diketones, oxalates *etc.*) is found.

OXAMIDE and *N,N'*-DIALKYLOXAMIDES

RNHCOCONHR

Symbol:	I	II	III	IV	V	VI
R:	H	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}

Symbol:	VII	VIII	IX	X
R:	C_6H_{13}	C_7H_{15}	C_8H_{17}	i-C_3H_7

Symbol:	XI	XII	XIII
R:	*sec*-C_4H_9	*tert*-C_4H_9	$C_6H_5CH_2$

Representative mass spectra are shown in Figs. 1 to 3 and the general fragmentation pattern is depicted in Scheme 1.

Both oxamide and *N,N'*-dialkyloxamides exhibit relative abundant molecular ions. In contrast, dialkyl oxalates are reported [3] to be very unstable upon ionization.

Cleavage of the bond between the two carbonyl groups is an important process, which in most cases gives rise to abundant ions, *a* (Fig. 1). Since all the oxamides investigated are symmetrical, *a* corresponds to half the molecular ion. Ion *a* decomposes by extrusion of CO or the elements of HNCO to give *b* and *c*, respectively. With increasing chain length of R, ion *b* maintains its importance, whereas the abundance of *c* (giving rise to the base peak in IV and V) rapidly decreases and is less than 2 % in IX. The reaction path leading to *b* closely corresponds to the predominant processes observed for acyclic α-diketones.[2a]

Whereas no hydrogen rearrangements are reported [2a] for α-diketones, oxamides give rise to three different types: (*i*) cleavage of the C—C bond between the two carbonyl groups with simultaneous migration of one hydrogen atom, (*ii*) McLafferty rearrangements with transfer of one or (*iii*) two hydrogen atom(s). Characteristic ions resulting from analogous McLafferty rearrangements are observed in the decomposition of the appropriate amides.[1,4]

Rearrangement (*i*) takes place preferentially for compounds with short substituent carbon chains giving rise to peaks corresponding to (*a*+H) and elimination of an alkyl isocyanate molecule. (The reversed charge distribution is to some extent also observed in the spectrum of I, $[HNCO]^+$). The predominant decomposition mode of the (*a*+H) ion is loss of CO, yielding the amine ion *d*.

The rearrangements (*ii*) and (*iii*) give rise to ions *e* and *f*, respectively. Type (*iii*) is observed in the fragmentation of IV to IX, XI and XII. It increases in importance with the

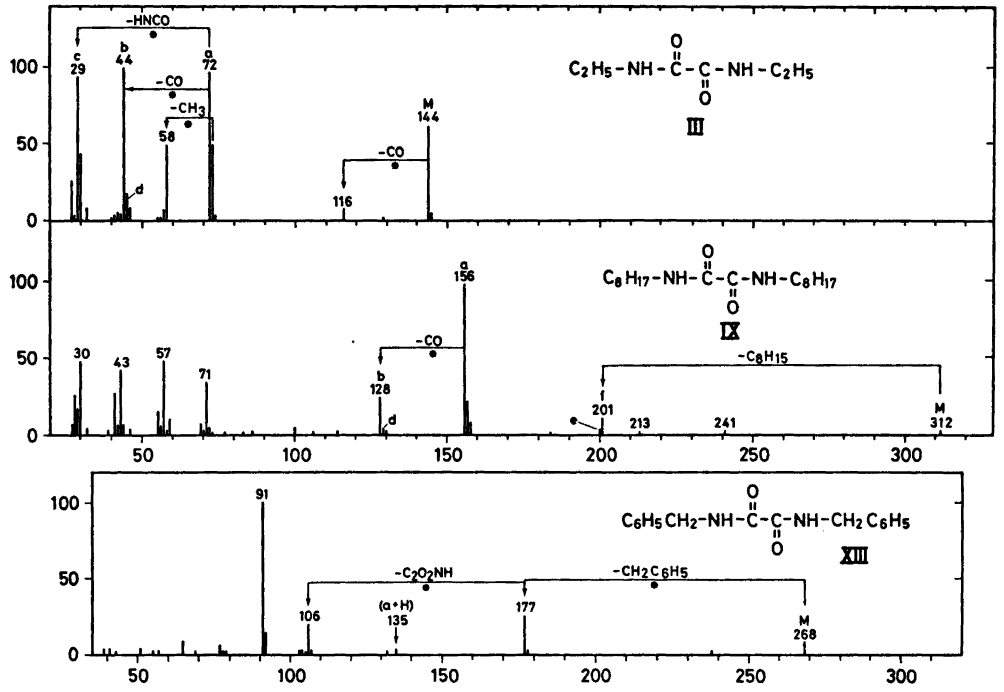


Fig. 1. Mass spectra of *N,N'*-diethyl-, *N,N'*-dioctyl- and *N,N'*-dibenzyloxamide.

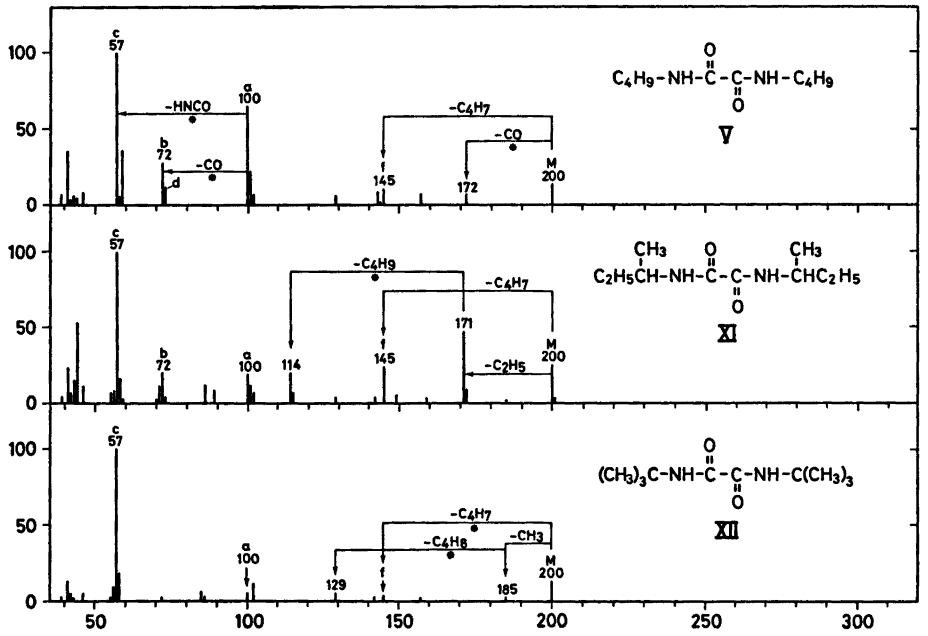
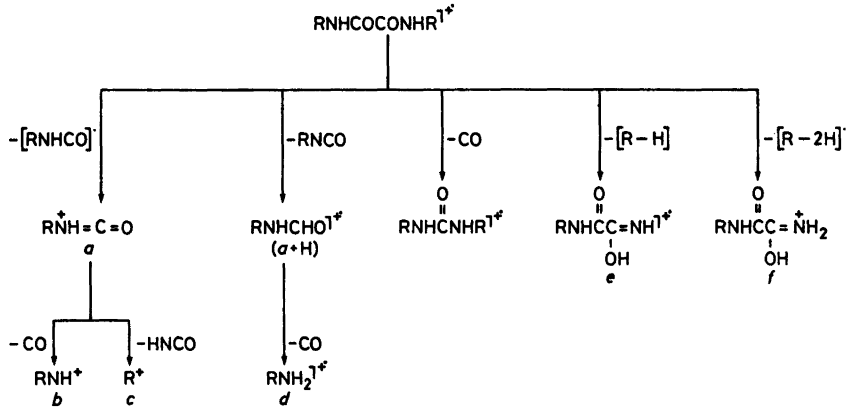


Fig. 2. Mass spectra of *N,N'*-dibutyl-, *N,N'*-di-*sec*-butyl- and *N,N'*-di-*tert*-butyloxamide showing the effect of branching at the α-carbon atom.



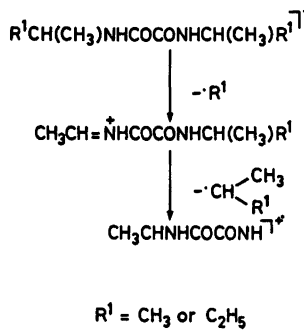
Scheme 1. (The fragmentations shown are supported by metastables).

chain length of the substituent (Figs. 1 and 2). The abundances of the ions resulting from (*ii*) are generally low.

Loss of CO from the molecular ions is a possible process for the compounds I to VII, X and XI. A corresponding extrusion is important for some of the oxalates [3] investigated, but is not observed for α-diketones.[2a]

Besides the fragmentation pattern outlined in Scheme 1, other decomposition modes gain importance, when the carbon chains are branched at the α-carbon atom (X to XII, Fig. 2). These are shown in Scheme 2 for compounds X and XI (R = *sec*-alkyl).

Further branching at the α-carbon atom in XII (R = *tert*-butyl) results in a remarkable decrease in importance of the decomposition paths shown in Scheme 1. In analogy to the fragmentation mode given in Scheme 2, a methyl group is lost from the molecular ion. However, further loss of an alkyl fragment is



$R^1 = CH_3$ or C_2H_5

Scheme 2.

in this case accompanied by a hydrogen rearrangement ($m/e = 129$, Fig. 2).

The well-known stability of the tropylium ion accounts for the unusual behaviour of XIII (R = benzyl) upon electron impact (Fig. 1).

N,N'-DIARYLOXAMIDES

R^2:	H	OCH_3	NO_2	Br
	XIV	XV: *o*-	XVIII: *o*-	XXI: *o*-
		XVI: *m*-	XIX: *m*-	XXII: *m*-
		XVII: *p*-	XX: *p*-	XXIII: *p*-

Representative spectra are shown in Fig. 3.

Loss of CO from the molecular ion of any *N,N'*-diaryloxamide is not detected. This is in contrast to the behaviour of most aliphatic oxamides and to results reported [3] for diaryl oxalates (showing abundant (60 – 100 %) $[M-CO]^+$ ions). However, the initial fragmentations connected with cleavage of the bond between the two carbonyl groups, yielding *a* and (*a*+H), are important in this series too (*cf.* Scheme 1). In the reaction path leading to (*a*+H), the reversed charge distribution is also observed, giving rise to (*a*+H) ions. This may be due to stabilization of the $[RNCO]^+$ ion by the aromatic substituent.[5] Elimination of CO from both *a* and (*a*+H), yielding *b* and *d*, respectively, normally takes place. The aromatic amine ion, *d*, is much more pronounced than the aliphatic analog, and gives rise to the base peak in the spectra of XIV to XVII,

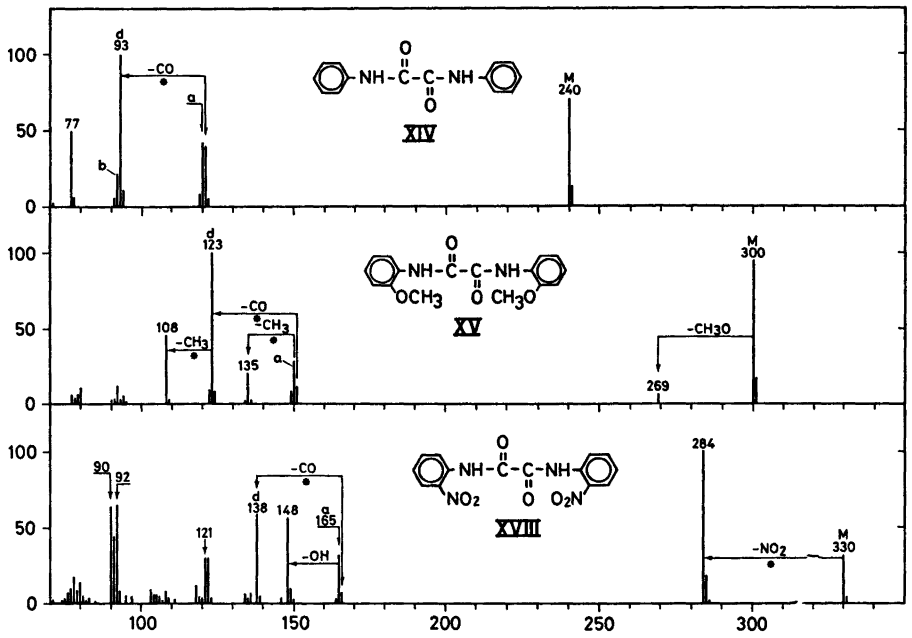
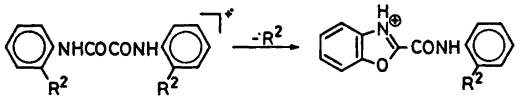


Fig. 3. Mass spectra of *N,N'*-diphenyl-, *N,N'*-di-*o*-methoxyphenyl- and *N,N'*-di-*o*-nitrophenyloxamide.

XXII and XXIII. As indicated by metastable peaks in the spectra of XV to XVII, *d* may also be formed directly from the molecular ion.

In addition decompositions specifically depending on the substituent R^2 take place. Thus, the molecular ions of the *ortho* substituted compounds eliminate $\cdot R^2$ and the following structure is proposed for the resulting ions.



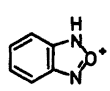
$R^2 = OCH_3$, NO_2 or Br.

The loss of a nitro or bromine radical from the molecular ions of XVIII and XIX, respectively, gives rise to the most abundant ions, whereas loss of the methoxy group is less pronounced (7 % in XV). Corresponding losses are not detected for the *meta*- and *para*-isomers.

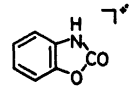
A noteworthy fragmentation process takes place for compounds with $R = NO_2$, in which cases *a* and (*a*+H) eliminate ·OH (followed by NO·) giving rise to peaks at $m/e = 148$ and 149, respectively. In the spectrum of the *ortho* isomer (XVIII, Fig. 3) the peak at $m/e = 148$ is the more abundant one, while the opposite is observed in the spectra of the two other isomers (XIX and XX). In these cases the modes of formation of the (*a*−OH) ions are rather dubious, and it is remarkable that loss of ·OH is not reported for ions corresponding to *a* formed in the fragmentation of α,α,α-trichloroacetanilides.[6] The decomposition modes of *a* derived from similarly substituted compounds in the two series are in all other respects analogous. Thus, the reported *ortho* effect involving expulsion of CO_2 (yielding $m/e = 121$) is also shown by *a* derived from XVIII. A corresponding process takes place from the (a+H) ion (yielding $m/e = 122$) and is supported by the presence of the appropriate metastable peak. However, ions with the same composition are exhibited also in the spectra of the *meta*- and *para*-isomers (XIX: 9 %, XX: 12 %). In these cases they may be formed exclusively in a two step process by successive losses of CO and O *via* the nitroaniline ion, *d* ($m/e = 138$). ($[M-O]^+$ ions are reported in the fragmentation of *m*- and *p*-nitroaniline [1]).

In correspondence with results reported for α,α,α-trichloroacetanilides, an *ortho* effect is also displayed in the decomposition of *a* in compounds with $R=OCH_3$ (XV to XVIII). Thus, the loss of a methyl group is only observed in the fragmentation of XV (Fig. 3). A corresponding process is not found for $(a+H)$.

The structure of the $[a-CO_2]^+$ and $[a-CH_3]^+$ ions resulting from interaction of the $-NHCO$ moiety with an *ortho* nitro- and methoxy substituent, respectively, have been ascribed [6] the structures shown below. Both include a five-membered ring containing at least one atom of the *ortho* substituent. Accordingly, no *ortho* effect of the bromine substituent in the decomposition of *a* is expected or observed. Loss of Br· takes place from *a* (and $(a+H)$) derived from the three isomers.



$a - CO_2^{+\cdot}$



$a - CH_3^{+\cdot}$

EXPERIMENTAL

The mass spectra were recorded on an AEI MS-902 mass spectrometer by Mrs. E. Wolff-Jensen, The H. C. Ørsted Institute, University of Copenhagen. The ion source temperature was typically 100 °C for the aliphatic and 180 °C for the aromatic substances (70 eV, direct sample insertion). The oxamides were prepared by a general method.[7]

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