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The mass spectra of furoxans have large  $\text{NO}^+$  peaks due to the fragmentation of the ring system at C-N and N-O bonds. Cleavage of the substituents and to a smaller extent ring fission at  $\text{C}_3\text{-C}_4$  account for other ion peaks. The spectra are sufficiently characteristic to serve for the identification of these compounds. The related furazans give different fragmentation patterns because carbon-carbon cleavage predominates.

Since the preparation of the first furoxan in 1880, various structures have been proposed for these compounds including the unsymmetrical ring structure I (2). In view of the chemical relationships between furoxans, glyoximes (II), and furazans (III) there is little doubt that furoxans are furazan oxides and the existence of structural isomers for unsymmetrical furoxans provides convincing arguments for an unsymmetrical structure. Recent evidence from crystal structure (3), infrared spectra (4), parachor values (4), and nuclear magnetic resonance spectra (5) has confirmed structure I for a number of compounds including I,  $\text{R} = \text{R}' = \text{Me}$  (6).

In the present investigation mass spectra have been determined for symmetrical I ( $\text{R} = \text{R}' = \text{Me}, \text{CF}_3, \text{C}_3\text{F}_7, \text{COOEt}, \text{Cl}$ ), one unsymmetrical compound ( $\text{R} = \text{Cl}, \text{R}' = \text{Me}$ ), and dimethylfurazan (Fig. 1-7). All these compounds give parent peaks which furnish precise molecular weights in agreement with structures I and III.

The mass spectrum of dimethylfurazan (Fig. 1) has large peaks for  $\text{CH}_3\text{-C}^+$  (base peak),  $(\text{M}-\text{CH}_3\text{CN})^+$ ,  $\text{CNO}^+$ ,  $\text{NO}^+$ ,  $\text{CH}_3^+$ ,  $\text{CN}^+$  (or  $\text{CH}_2\text{C}^+$ ),  $\text{CH}_3\text{C}_2^+$ , and  $\text{CH}_3\text{CN}^+$ . A small peak at  $m/e$  68, which could be regarded as furazan ion has been assigned to the isotopically favored ion  $(\text{M}-\text{NO})^+$  (The  $m/e$  69/68 ratio is 0.0426 suggesting a  $\text{C}_4$  fragment as opposed to a  $\text{C}_2$  fragment). There is thus no evidence for the intact ring system in the fragments. At least one mode of cleavage yields  $\text{MeCNO}^+$  and  $\text{MeCN}^+$  and most of the other fragments also can result from ring fission at  $\text{C}_3\text{-C}_4$  (7).

All furoxans, on the other hand, give large peaks of mass 30 which have been identified as  $\text{NO}^+$ . The  $\text{NO}^+$  peak is in fact the base peak in the investigated furoxans with the exception of dicarbethoxyfuroxan, which has a higher peak of mass 29 due to  $\text{C}_2\text{H}_5^+$  from ester cleavage. The furoxans give positive ion fragments corresponding to  $(\text{M}-\text{NO})^+$ ,  $(\text{M}-\text{N}_2\text{O}_2)^+$ , and  $\text{N}_2\text{O}_2^+$  plus others which arise from the tendency of specific sub-

stituents to split off as substituent ions and other fragments but there are only small ion peaks which can be ascribed to carbon-carbon cleavage in the ring system. Methyl substituents tend to split off as  $\text{Me}^+$  but also give rise to ions containing  $\text{CH}_2$ ,  $\text{CH}$ , and  $\text{C}$ . Chlorine substituents become  $\text{Cl}^+$  and occur in ions such as  $\text{ClC}^+$  and  $\text{ClC}_2^+$ , while  $\text{CF}_3$  groups furnish  $\text{CF}_3^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}^+$ , and  $\text{F}^+$  fragments. Fluoroalkylfuroxans give in addition  $(\text{M}-\text{FN}_2\text{O}_2)^+$  and  $(\text{M}-\text{F})^+$  ions. The case of  $\text{C}_3\text{F}_7$  substituents is much more complex than  $\text{CF}_3$  because of the numerous fluorine-containing fragments from  $\text{C}_1$  to  $\text{C}_5$ . Possibly the ring system is more stable in this case and in the chloro compounds because there is a small peak at  $m/e = 84$  in their mass spectra which is assigned to the  $\text{C}_2\text{N}_2\text{O}_2^+$  ion. (A very small peak at  $m/e = 84$  in the spectrum of chloromethylfuroxan is not displayed in Fig. 3.)

The mass spectrum of dicarbethoxyfuroxan (Fig. 7) is different from those of the other furoxans because the substituent groups undergo cleavage more easily than the ring system. Thus the base peak is  $\text{C}_2\text{H}_5^+$  rather than  $\text{NO}^+$  and there are peaks for  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{C}_2\text{H}_4^+$ ,  $\text{C}_2\text{H}_5\text{O}^+$ , and  $(\text{M}-\text{C}_2\text{H}_5\text{O})^+$  which can be traced to the fragmentation of the carbethoxyl group. A base peak of  $m/e = 29$  is unusual for ethyl esters and the overall pattern makes dicarbethoxyfuroxan resemble aromatic rather than aliphatic esters. Ring cleavage accounts for  $\text{NO}^+$ ,  $(\text{M}-\text{NO})^+$ , and the ion at  $m/e = 100$  which has been identified as  $(\text{M}/2-\text{CH}_3)^+$ . In common with other negatively substituted furoxans there is a  $\text{C}_2\text{N}_2\text{O}_2^+$  ion ( $m/e = 84$ ) but it is more abundant in this case. An ion at  $m/e = 130$  is assigned to furoxancarboxylic acid which is believed to be formed by hydrogen transfer. The assignment of other ions at  $m/e = 158$  ( $\text{M}-\text{C}_2\text{H}_4\text{CO}_2$ ) $^+$  and  $m/e = 86$  as monocarbethoxyfuroxan and furoxan is consistent with the hydrogen transfer mechanism.

There is little evidence for unimolecular dissociation

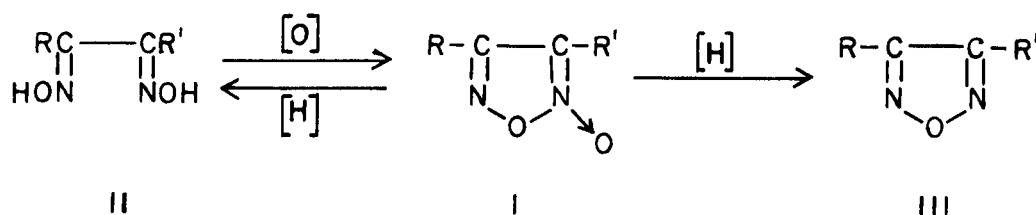


Figure I

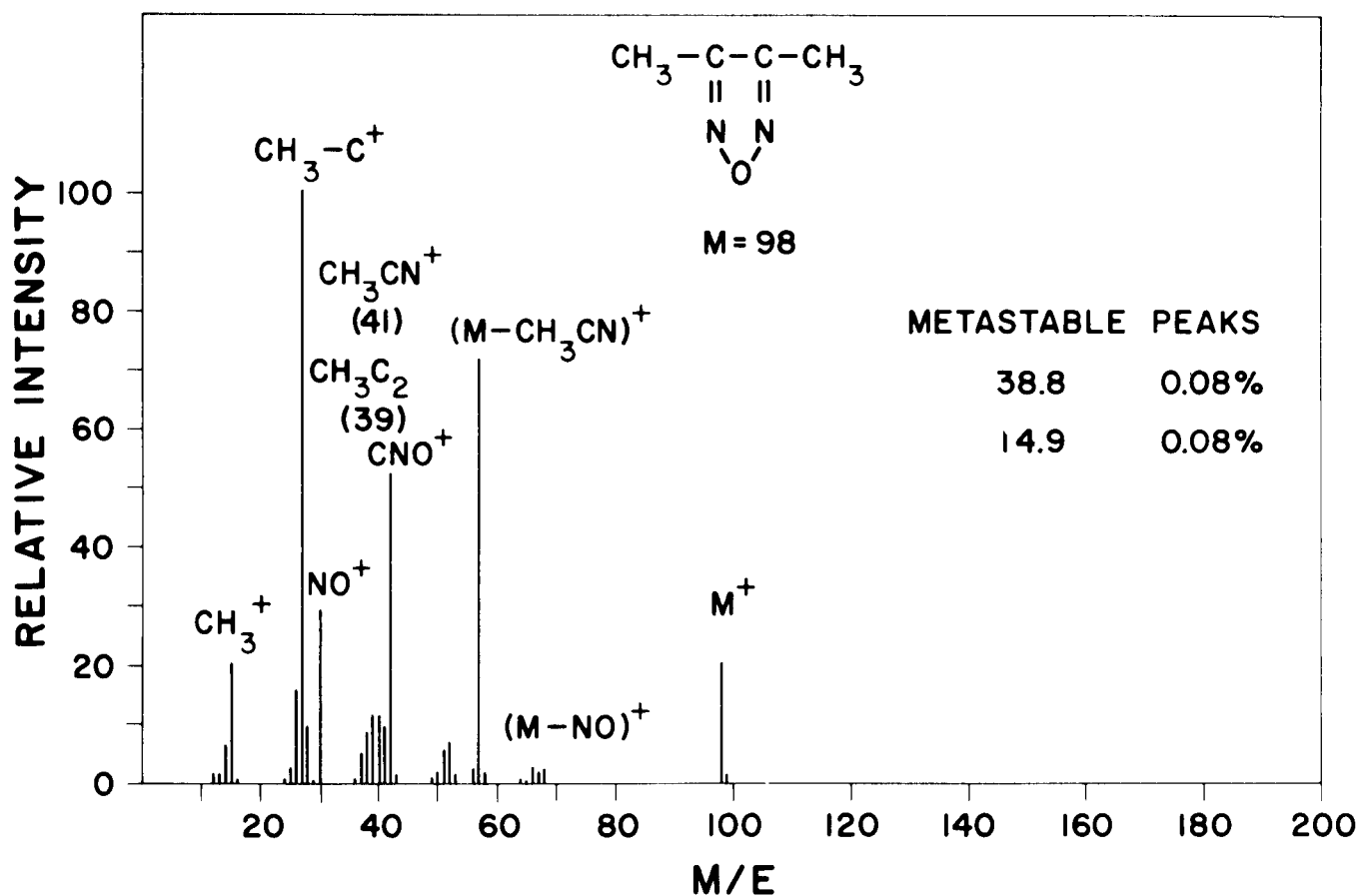


Figure II

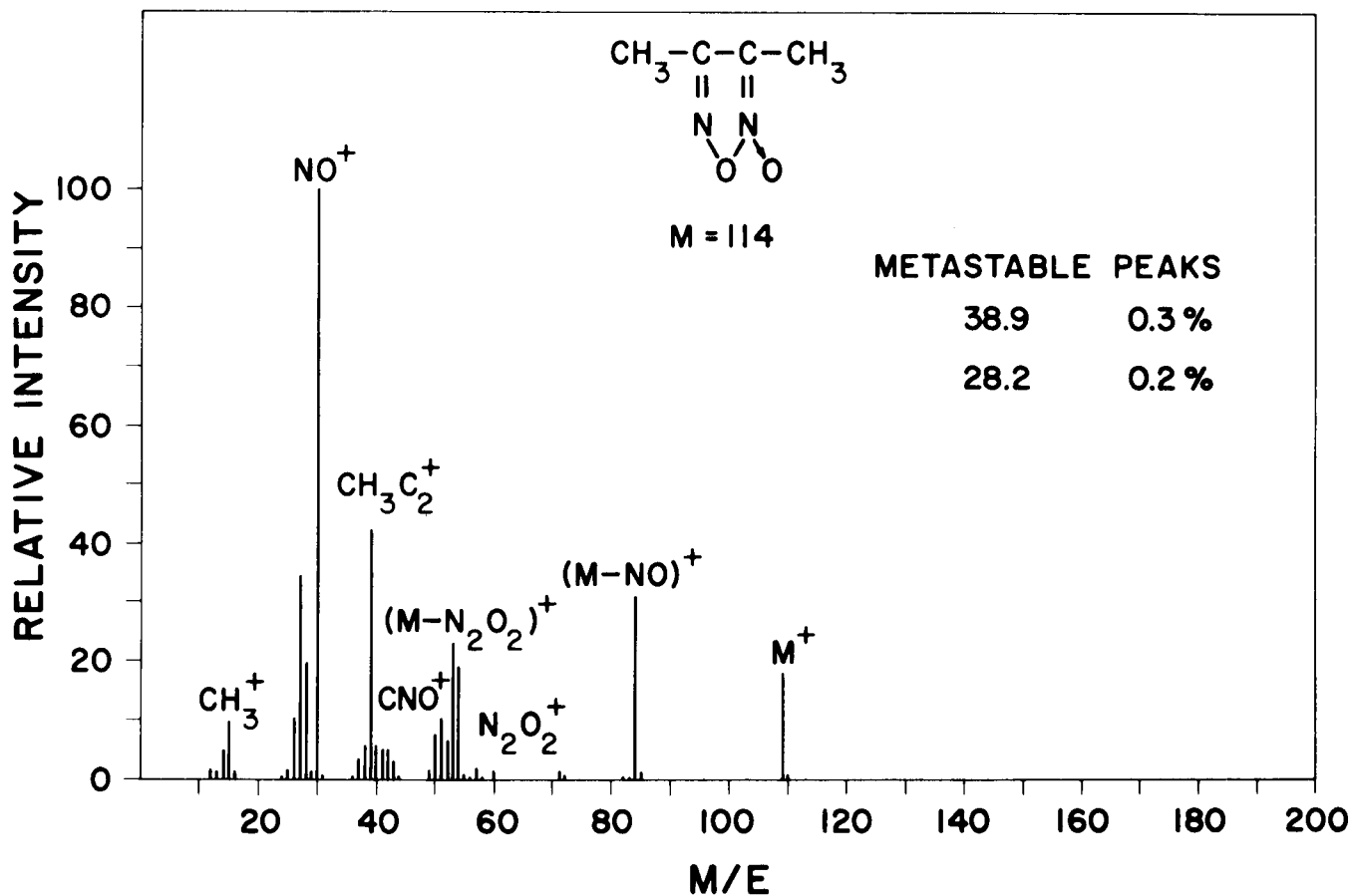


Figure III

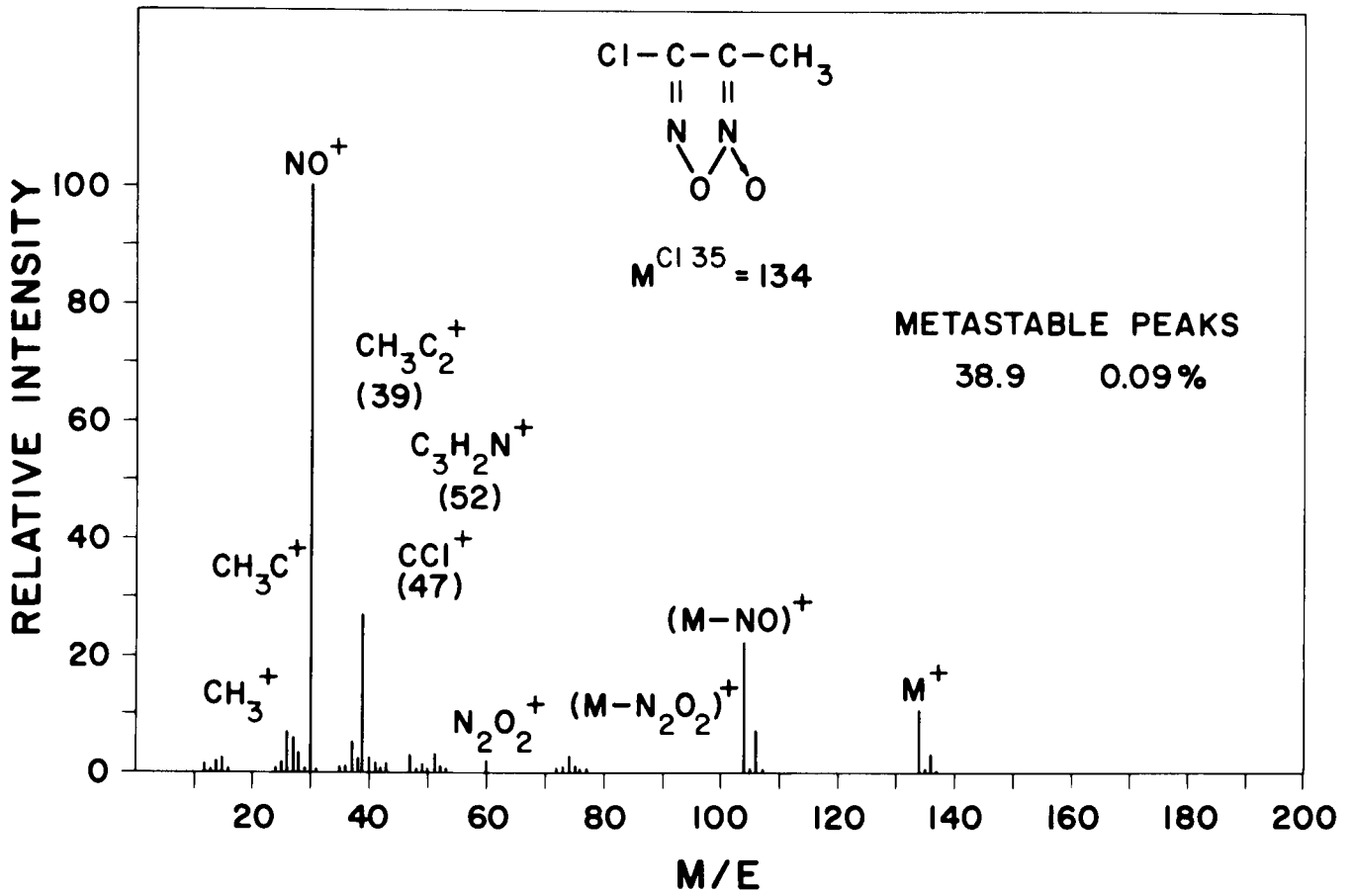


Figure IV

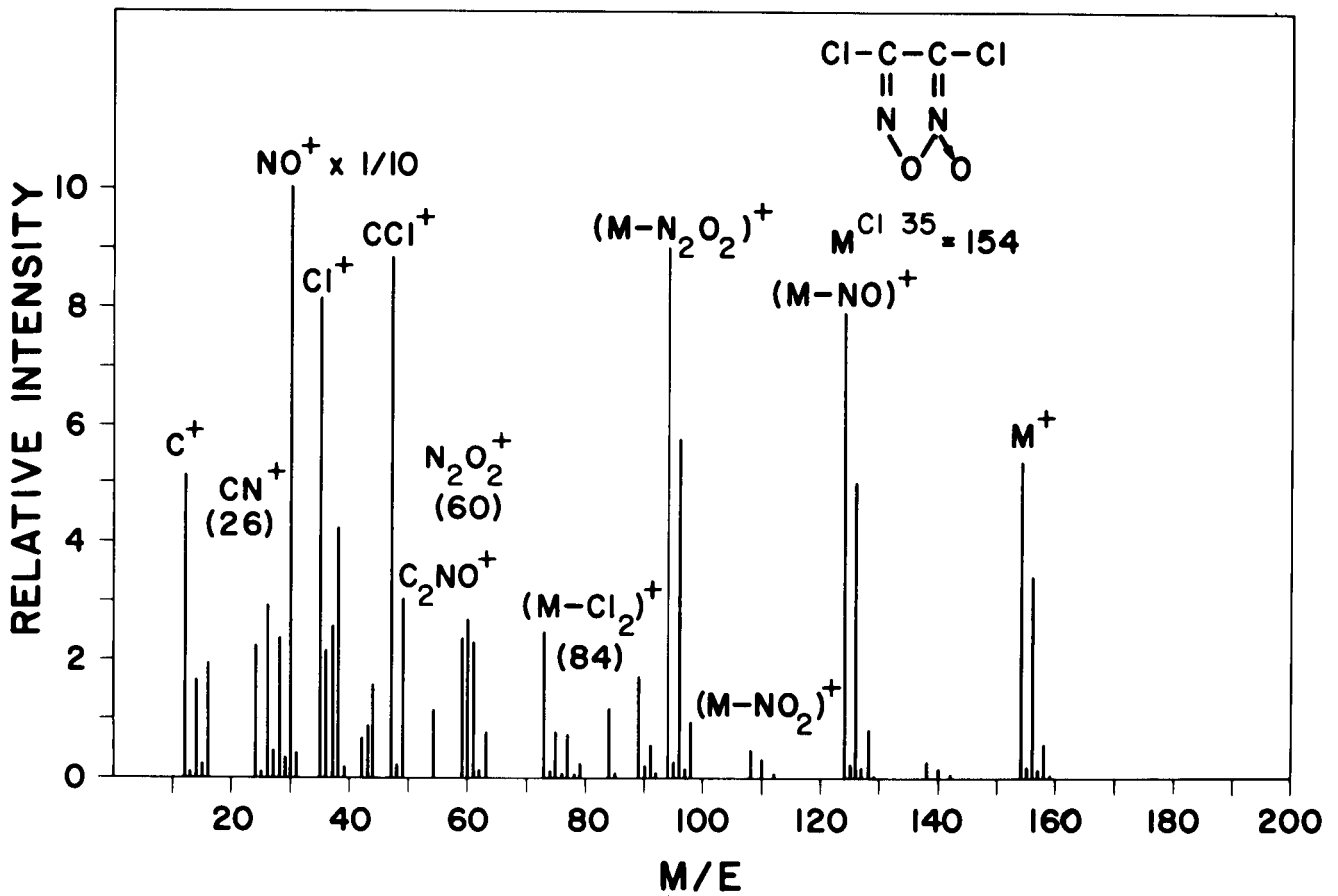


Figure V

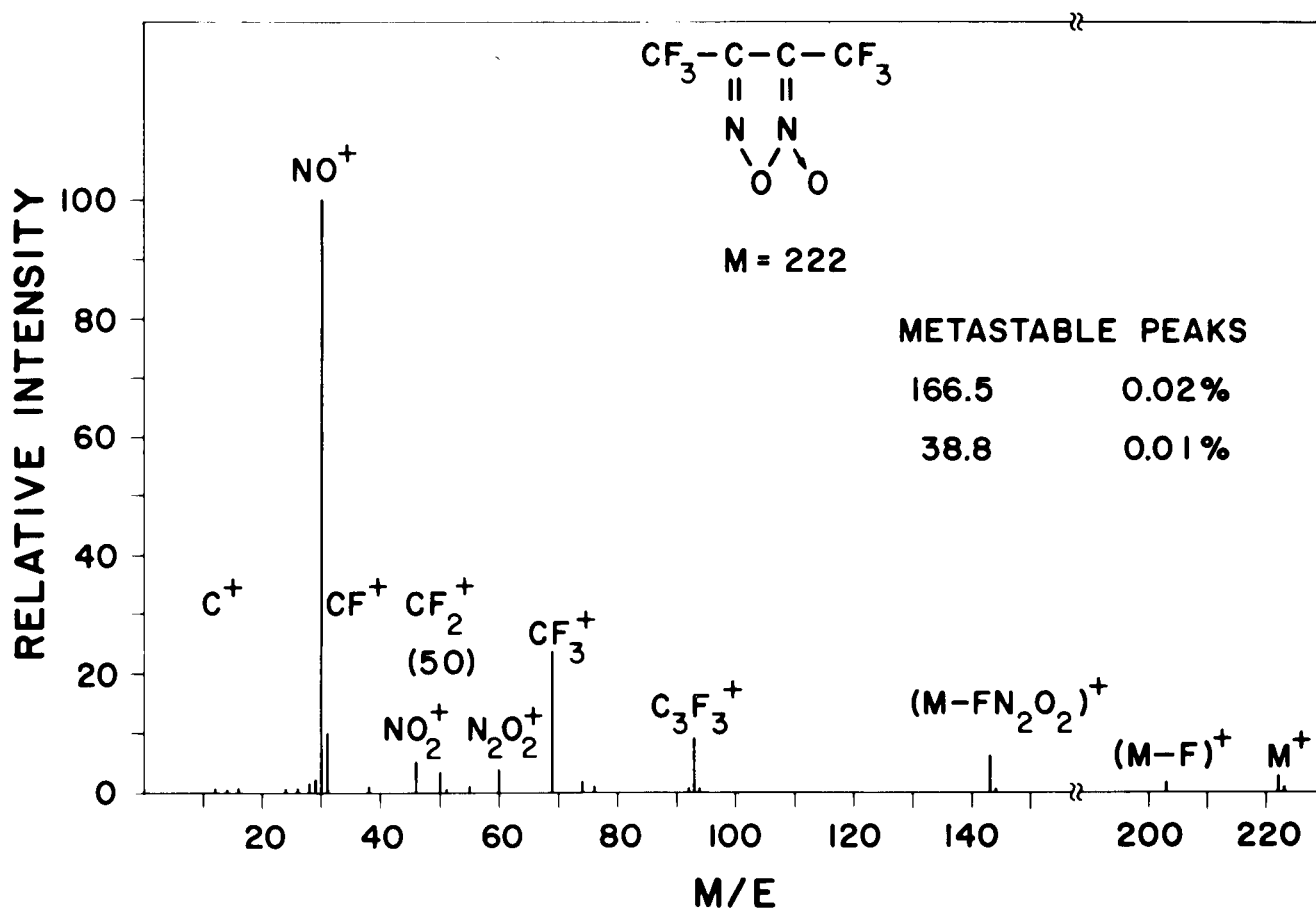


Figure VI

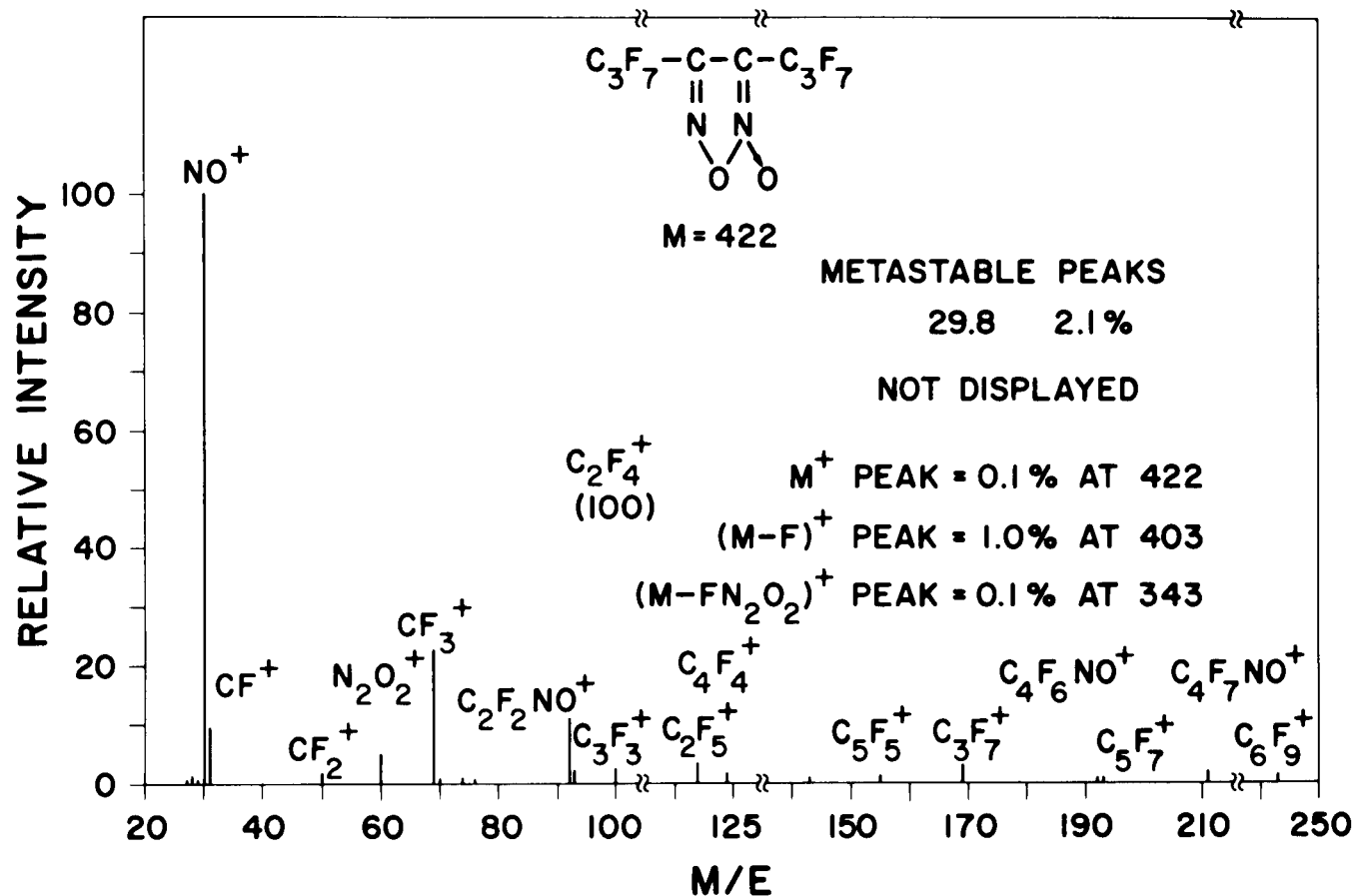


Figure VII

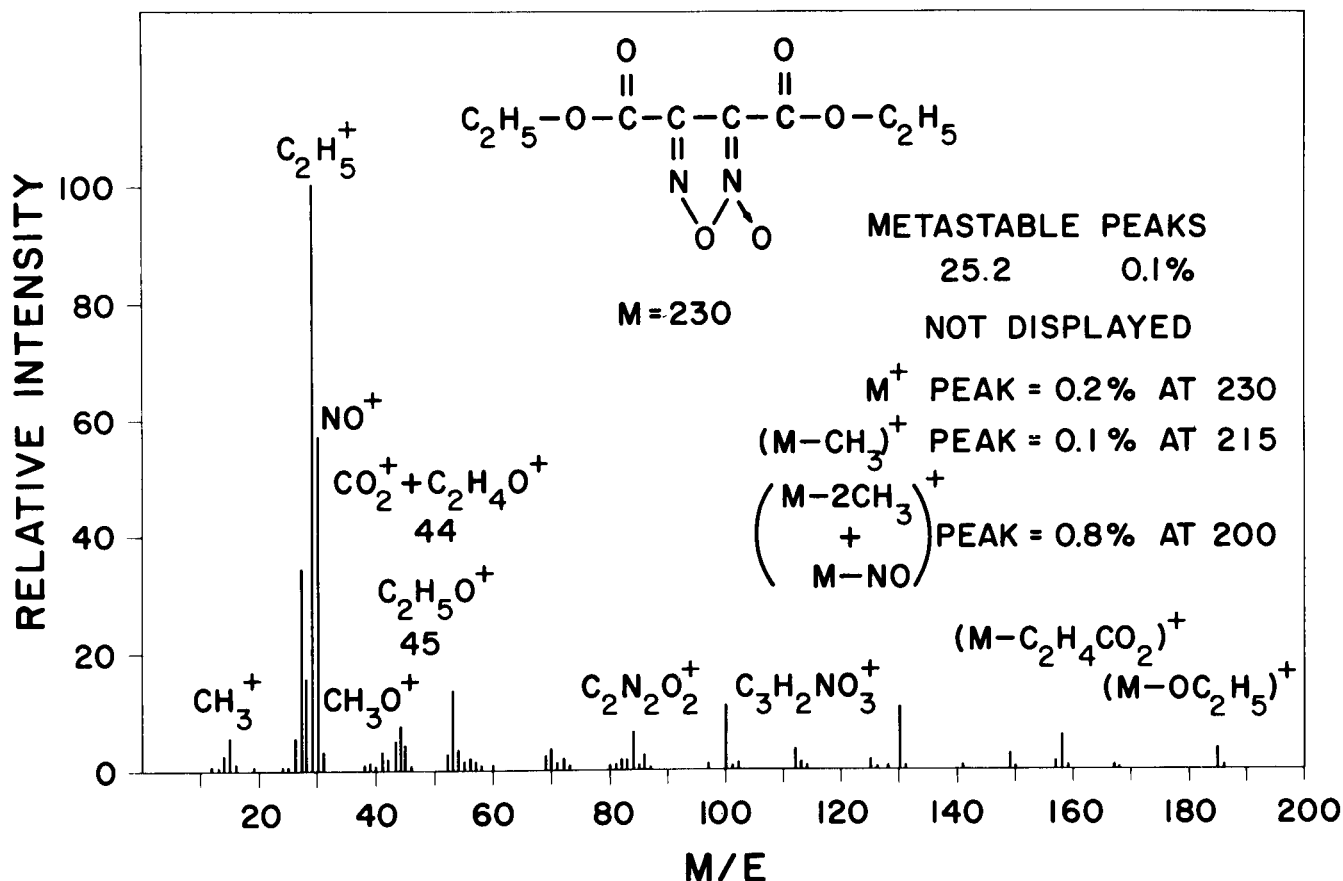


TABLE I

Sensitivity and Total Ionization Data

Compound	$\text{M}^+$ (a)	Base peak m/e	Sensitivity (b)	$\Sigma$ % RI (c)
$\text{Me}_2\text{C}_2\text{N}_2\text{O}$	98	27	100	413
$\text{Me}_2\text{C}_2\text{N}_2\text{O}_2$	114	30	100	388
$\text{MeClC}_2\text{N}_2\text{O}_2$	136 (d)	30	148	236
$\text{Cl}_2\text{C}_2\text{N}_2\text{O}_2$	158 (d)	30	170	209
$(\text{CF}_3)_2\text{C}_2\text{N}_2\text{O}_2$	222	30	212	182
$(\text{C}_3\text{F}_7)_2\text{C}_2\text{N}_2\text{O}_2$	422	30	200	179
$(\text{COOEt})_2\text{C}_2\text{N}_2\text{O}_2$	230	29	169 (e)	345
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	58	43	112	344

(a)  $\text{M}^+$  = m/e of parent peak. (b) Units are chart divisions of base peak per micron of sample pressure. (c) % Relative intensity is based on the most intense peak in the spectrum (base peak) = 100%. The summation neglects peaks smaller than 0.1% and others which are obvious impurities, *e.g.* traces of solvents. Sensitivity  $\times$   $\Sigma$  % RI is proportional to the total number of positive ions formed per micron of sample pressure. (d) Peaks for  $\text{M}^{\text{Cl}} = 35$  were observed at 134, 154, and 156 respectively. (e) Varies slightly with pressure. The quoted value is for sample pressures of 10-30 microns.

of furoxans and little fragmentation to give RCNO ions (8).

Since all the investigated furoxans undergo the same type of fragmentation as the authentic dimethyl compound, have similar ultraviolet and infrared spectra, and undergo reactions characteristic for furoxans, their structures may be regarded as established.

#### EXPERIMENTAL

##### Materials.

The investigated compounds were analytically pure specimens. Their preparation and properties have been described previously (9,10,11).

##### Mass Spectra.

Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-103 mass spectrometer, modified to make it equivalent to a Model 21-103C. The conventional dual collector slit of the 21-103C analyzer was replaced by a single 15-mil slit and the metastable suppressor circuit was modified slightly for excess kinetic energy studies.

All spectra were recorded at 70V ionizing voltage and 15  $\mu$ A ionizing current. Magnet currents were 0.775A for all runs except the diperfluoropropylfuroxan, for which a current of 1.0A was used. Mass peaks between  $m/e = 12$  and  $m/e = 24$  were obtained with a 0.5A magnet current and the heights adjusted to correspond to the higher amperage scan by using the ratio  $\frac{m/e \ 30 \ (0.5A)}{m/e \ 30 \ (x \ A)}$

The furoxans were sampled as liquids with the CEC liquid gallium-sintered disk liquid inlet system, heated to 50° (12). Pressures were measured in a 3 l. expansion volume with a micromanometer. The temperature of the Isatron (ion source) was 250  $\pm$  0.5°.

The pertinent sensitivity and total ionization data are given in Table I and are compared with similar data for butane, which was run under the same conditions.

#### REFERENCES

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- (7) Similar results have been announced recently by R. A. Olofson and J. S. Michelman, Abstracts of the 145th Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 63Q.
- (8) It was proposed by Skinner, *J. Am. Chem. Soc.*, **46**, 731 (1924), on the basis of cryoscopic measurements, that dicarbethoxyfuroxan is completely dissociated in benzene to the nitrile oxide EtOCOCNO, from which it is readily prepared. A similar dissociation may occur under the conditions of temperature and pressures existing in the mass spectrometer ion source at low sample pressure since the relative abundance of the ions containing the ring system decreases slightly at sample pressures below 10  $\mu$ . It has been established now that such dissociation does not occur in benzene. The infrared spectra of dicarbethoxyfuroxan are identical in benzene and in pure liquid except for minor shifts [ $\lambda$  C=O (liq) 5.69,  $\lambda$  C=N (liq) 6.13,  $\lambda$  C-O (C<sub>6</sub>H<sub>6</sub>) 5.69,  $\lambda$  C N (C<sub>6</sub>H<sub>6</sub>) 6.12  $\mu$ ] and there is no band in the 4.36  $\mu$  region which is characteristic for nitrile oxides [R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960)]; furthermore, using Skinner's experimental data, the authors calculate a molecular weight of 210 rather than 119.
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- (12) A temperature of 90° was used to obtain higher sample pressures of dicarbethoxyfuroxan.

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