MASS SPECTRA OF PHENOXAZONES

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Mass spectra of phenoxazones have been recorded and interpreted using metastable peaks and measurements with high resolution power. Basic fragmentation of phenoxazones is both successive elimination of CO, CO + H•, HCN and successive elimination of two carbonyl groups and HCN.

Within a complex investigation of phenoxazones we have measured their mass spectra which are not available in literature. Out of cognate compounds spectra of substituted oxazoles were published[1-3].

RESULTS

The measured mass spectra were analyzed by means of metastable peaks and measurements at high resolution power. The basic fragmentation can be demonstrated with the non-substituted phenoxazone-3 (Scheme 1, top of Fig. 1). The molecular ion splits off first carbon monoxide and then successively both neutral fragments CO + H•, HCN and CO, HCN. It is presumed that the split off hydrogen comes from the fourth carbon atom, *i.e.* carbon atom located between carbonyl group and the carbon carrying ether linkage. The presumption is supported by the elimination taking place in all the other phenoxazones which have the remaining aromatic hydrogen atoms of the basic skeleton substituted by benzene nuclei. It is presumed, too, that the ion formed by simultaneous elimination of CO + H• is rearranged[4,5] to give benzodehydroazatropylium which, in turn, splits off HCN. Besides the described fragmentation there proceeds another splitting of phenoxazone which is, however, still less marked, *i.e.* elimination of CO, C_2H_2, CO and HCN – see the ions with *m/e* values 169, 115 and 88.

Fragmentation of the phenoxazones substituted by one or two benzene nuclei is analogous to that of the non-substituted phenoxazone-3. The isomers benzo[*a*]phenoxazone-10, benzo[*a*]-phenoxazone-9 and benzo[*a*]phenoxazone-5 cannot be well

differentiated by their mass spectra, it is, however, possible to decide whether the connected benzene nucleus is located at the aromatic ring without carbonyl group, since in this case the spectrum contains an intensitve peak m/e 114 corresponding to the ion C_9H_6 which is formed by elimination of the fragment C_4H_2 from the ion m/e 164. Also the isomers dibenzo[a,h]phenoxazone-5 and dibenzo[a,j]phenoxazone-5 are indiscernible by their mass spectra. Substitution by amino group as in benzo[a] 5-aminophenoxazone-9 has also only a slight influence: the ions formed

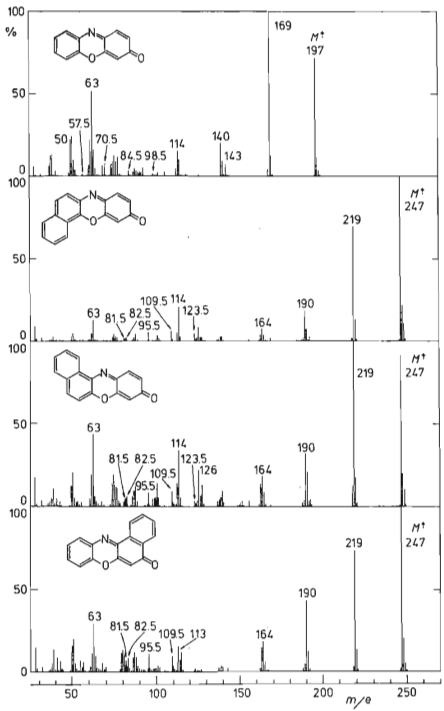
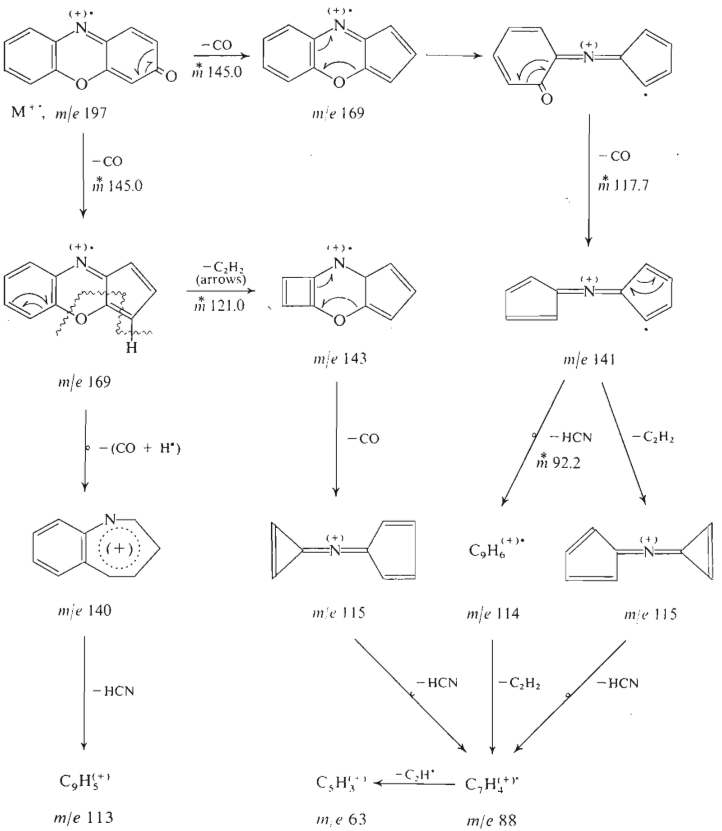


FIG. 1

Mass Spectra of Phenoxazone-3, Benzo[a]phenoxazone-10, Benzo[a]phenoxazone-9 and Benzo-[a]phenoxazone-5

on elimination of HCN (*m/e* 178, 179) (Scheme 1) split off another HCN from the amino group to give ions *m/e* 151 and 152.



SCHEME 1

The most complex fragmentation is observed in the case of benzo[*a*]9-ethoxyphenoxazine-5 (see Scheme 2 and the bottom of Fig. 2). Splitting of this compound proceeds in two sequences. In the first one ethylene is split off from ethoxyl group and then successively CO and CO + H$^{\bullet}$; phenolic hydroxyl group is tautomerized to keto form whereupon CO is eliminated to give the ion *m/e* 178 which splits off HCN (*m/e* 151). In the second sequence ethylene oxide is split off from ethoxyl group, and the formed benzo[*a*]phenoxazonium ion is split in the same way as

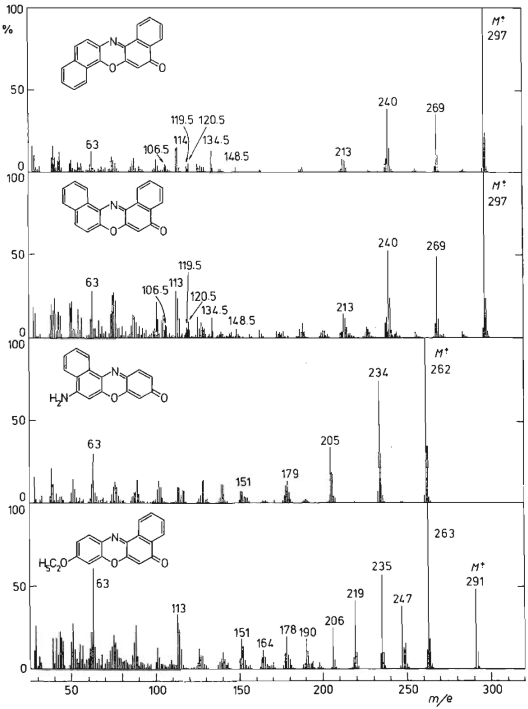
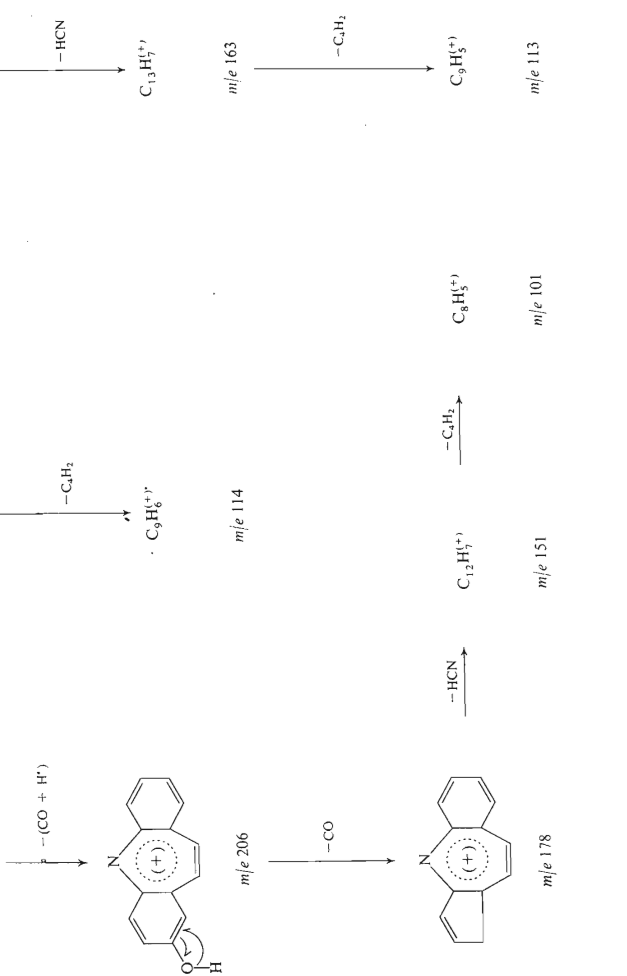


FIG. 2

Mass Spectra of Dibenzo[*a,h*]phenoxazone-5, Dibenzo[*a,j*]phenoxazone-5, Benzo[*a*]5-aminophenoxazone-9 and Benzo[*a*]9-ethoxyphenoxazone-5

M+·, m/e 291
−C2H4
m* 237.8
m/e 263
−CO
m* 210.0
m/e 235
M+·, m/e 291
−C2H4O
m* 209.6
m/e 247
−CO
m/e 219
−(CO + H·)
m/e 190
−CO
(arrows)
m/e 191
−HCN
C13H8+·
m/e 164


−(CO + H·)
−CO
m/e 206
m/e 178
−HCN
C12H7(+)
m/e 151
−C4H2
C8H5(+)
m/e 101
−C4H2
C9H6(+·)
m/e 114
−HCN
C13H7(+)
m/e 163
−C4H2
C9H5(+)
m/e 113

SCHEME 2

it is given in Scheme 1, *i.e.* successive elimination of CO, CO + H$^{\cdot}$, HCN and CO, CO and HCN.

All the measured phenoxazones gave intensive molecular peaks, which is in accordance with their stable aromatic structure, a series of ions with double charges being observed, too. Fragmentation rate of the molecular ions increased with increasing number of nuclei, depending also on their position: dibenzo[*a*,*h*]phenoxazone-5, dibenzo[*a*,*j*]phenoxazone-5, benzo[*a*]-phenoxazone-10, benzo[*a*]phenoxazone-5, benzo[*a*]phenoxazone-9, phenoxazone-3.

EXPERIMENTAL

Phenoxazone-3 was prepared by oxidation of phenoxazine[8]. Benzo[*a*]phenoxazone-9 was prepared by reaction of *p*-nitrosophenol with 2-naphthol[9]. Benzo[*a*]-phenoxazone-5 was prepared by reaction of *o*-aminophenol with 2-hydroxy-1,4-naphthoquinone[10]. Benzo[*a*]phenoxazone-10 was prepared from 2-nitroso-1-naphthol and resorcinol[11]. Dibenzo[*a*,*j*]phenoxazone-5 was prepared by reaction of 1-nitroso--2-naphthol with 2-naphthol[10]. Dibenzo[*a*,*h*]phenoxazone-5 was prepared by reaction of 2-nitroso-1-naphthol with 2-naphthol[12]. Benzo[*a*]5-aminophenoxazone-9 was prepared by reaction of benzo[*a*]phenoxazone-9 with hydroxylamine hydrochloride[9]. Benzo[*a*]9-ethoxyphenoxazone-5 was prepared from benzo[*a*]phenoxazone-9 by heating in ethanol with addition of hydrochloric acid[9].

The mass spectra of the phenoxazones were obtained at electron energy 70 eV in a mass spectrometer AEI MS 902 with direct inlet. For the individual substances the temperature of the ion source varied within 140 to 240°C. The metastable peaks given in the Schemes were observed in low resolution spectra. All the fragmentation transitions were proved by the methods DADI (Direct Analysis of Daughter Ions)[13] and MIKES (Mass Analyzed Ion Kinetics Spectroscopy)[14] using a mass spectrometer Varian MAT 311.

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REFERENCES

1. Bowie J. H., Donaghue P. F., Rodda H. J., Cooks R. G., Williams D. H.: Org. Mass Spectrom. *1*, 13 (1968).
2. Crow W. D., Hodgkin J. H., Shannon J. S.: Aust. J. Chem. *18*, 1441 (1965).
3. Lunguist R. T., Ruby A.: Appl. Spectrosc. *20*, 258 (1966).
4. Robertson A. V., Djerassi C.: J. Amer. Chem. Soc. *90*, 6992 (1968).
5. Barnes C. S., Occolowitz J. L.: Aust. J. Chem. *17*, 975 (1964).
6. Acrel T., Lumpkin H. E.: Anal. Chem. *32*, 1819 (1960).

7. Benyon J. H., Lester G. R., Williams A. E.: J. Chem. Phys. *63*, 1861 (1959).
8. Kehrmann F., Saager A.: Ber. *35*, 341 (1902).
9. Fisher O., Hepp E.: Ber. *36*, 1806 (1903).
10. Kehrmann F.: Ber. *28*, 353 (1895).
11. Dostál V., Haviger A.: Sb. Pedagog. Fak. Univ. Palackého, Matematika-Chemie, Olomouc *1972*, 129.
12. Ružička E., Dostál V.: Monatsh. Chem. *99*, 1915 (1968).
13. Maurer K. H., Brunee C., Kappus G., Habfast K., Schroder U., Schulze P.: 19th Conf. on Mass Spec., Paper K-9, Atlanta 1971.
14. Benyon J. H., Cooks R. G.: Res./Develop. *26*, Nov. (1971).

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