

MASS SPECTROMETRY OF ONIUM COMPOUNDS—IV:*

DIAZONIUM SALTS

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Abstract—The zwitterions of diazotized *ortho* and *para* aminophenol are very volatile and give strong peaks in the mass spectra corresponding to the molecular ion. The *m*-isomer, which cannot be stabilized through a simple quinonoid structure, gives rise to a complex spectrum through decomposition and coupling reactions. The zwitterions of diazotized anthranilic and sulphanilic acids did not give the molecular ion peak.

OUR INTEREST in *N*-quaternary salts and betaines thereof¹ have led us to investigate the behaviour of simple aromatic diazonium salts in the mass spectrometer. Mass spectrometric studies of diazonium salts have so far been restricted to diazoketones and diazomethane derivatives^{2 to 5} and to the generation of benzyne intermediates from diazocarboxylates under special conditions.⁶ We have studied the diazotized aminophenols, *o*-anthranilic acid and *o*-sulphanilic acid.

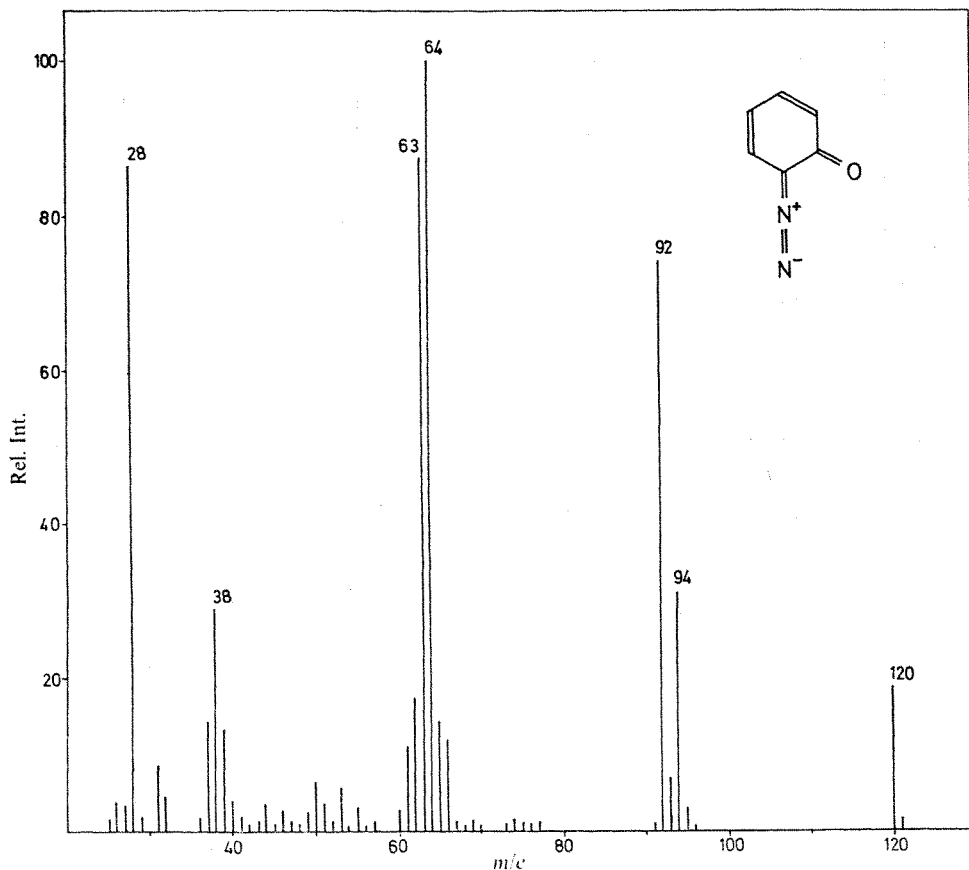


FIG. 1

* For Part III, see ref. 1.

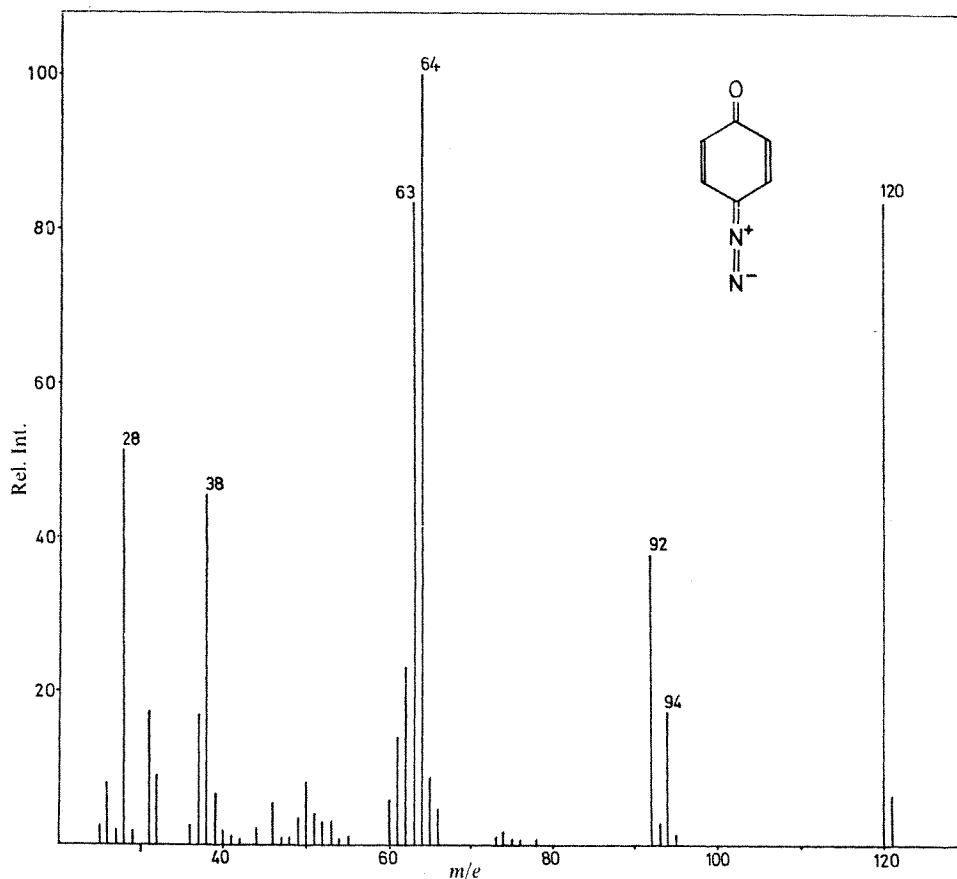
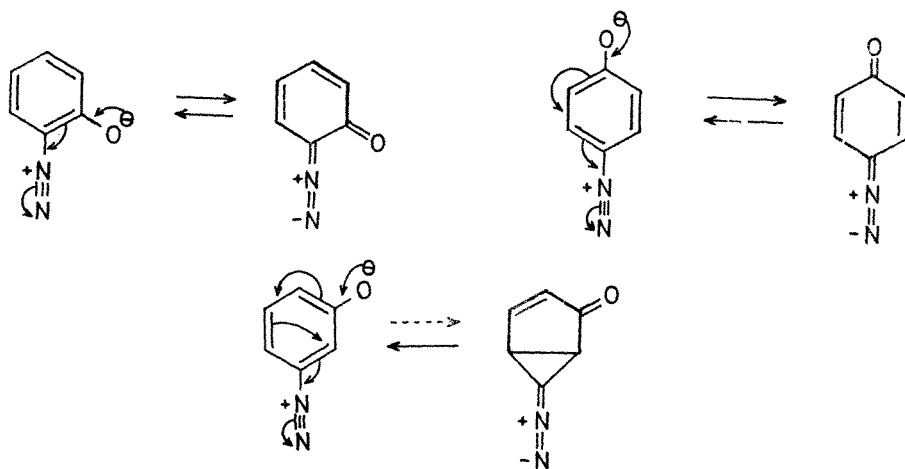
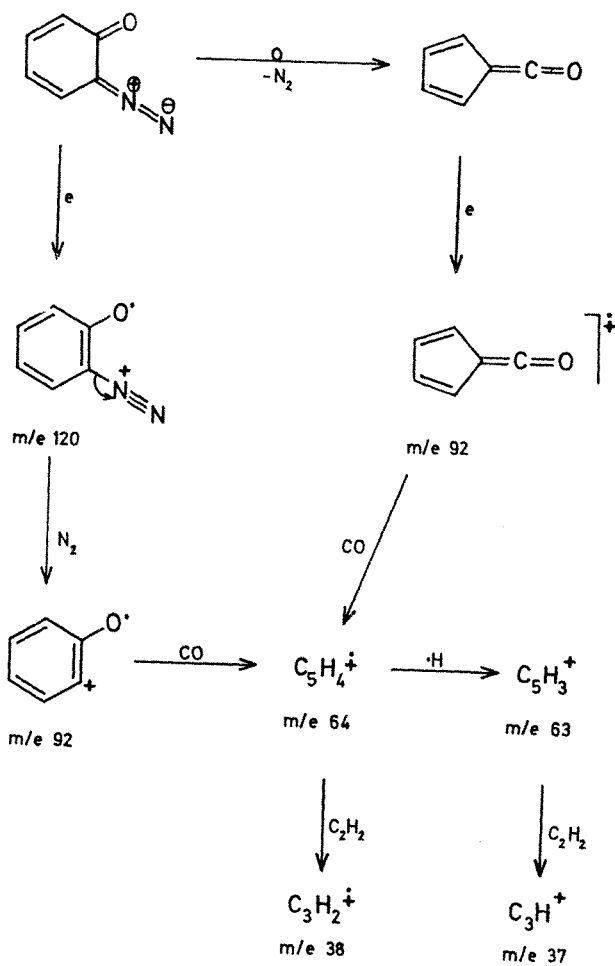


FIG. 2.

The chlorides of the diazotized aminophenols showed marked differences. The thermally unstable *meta* isomer initially gave the spectrum of *m*-chlorophenol with peaks gradually appearing at *m/e* 220, *m/e* 312 and *m/e* 404, which arise from the coupling products between chlorophenol and unreacted diazonium salt. No peak due to HCl loss and formation of the zwitterion could be detected. The spectra of the *ortho* and *para* isomers were qualitatively very similar. Thermal chloride ion substitution of the diazonium group with chlorophenol formation only gave rise to a weak signal from the chlorophenol in the spectra. Instead the main pyrolytic pathway was loss of HCl with formation of the zwitterion. For comparison the *ortho* and *para* diazo-oxides were prepared and found to give the same mass spectra as their hydrochlorides except for the absence of chlorophenol and HCl. The strong signal from the molecular ions of the *ortho* and *para* isomers is explained by the possibility for these isomers to exist in non-charged quinonoid structures. A covalent form of the *meta* isomer would involve formation of a bicyclic keto structure rather similar to the valence isomeric structure used to explain the volatility of pyridinium-3-oxides.¹ Energetically, however, the mass spectra show that substitution of the diazonium group is favoured.



SCHEME 1



SCHEME 2

The quinonoid form of the *ortho* and *para* isomers is supported by i.r.-spectroscopy and by dipole measurements, and it is stated that the *ortho* isomer is more 'quinonoid' than the *para* isomer.⁷ The quinonoid formulation is in accordance with the high vapour pressure observed, especially for the *ortho* isomer. Thus it was difficult to run the latter by direct insertion even with the source temperature at 50°. The high volatility observed could be used for purification. Thus preparative sublimation of the *o*-isomer was run at 50°/0.1 torr. The *p*-isomer could be sublimed at 80°/0.015 torr, but occasionally the sample blew up so that the experiment should be run on a small scale.

The mass spectra of the *ortho* and *para* isomers resemble those described for diazoketones.^{2,3,4} A characteristic feature is loss of nitrogen, either thermally or by electron-impact. The latter process was confirmed by a metastable transition for the loss of 28 mass units from the molecular ion. Thermal nitrogen expulsion is confirmed by variable relative intensity of the m/e 92 [$M - N_2$] peak and of the variable and initially very intense N_2 (m/e 28) peak. The thermal loss of nitrogen is best explained by a Wolff rearrangement as shown for 2-diazoindane-1,3-dione.⁴

Both the zwitterions and their hydrochlorides exhibit a peak of variable relative intensity at m/e 94 with composition C_6H_6O which fragments as phenol. A similar peak has been observed in the spectrum of 2-diazoindane-1,3-dione.⁴ Its genesis is suggested as being due to hydrogen radical extraction from the source walls by the product formed on thermal loss of nitrogen.⁴ When the instrument was saturated with deuterium oxide, however, the m/e 94 peak was shifted only one mass unit higher so that the origin of phenol is still obscure.

o-N,N,N-Trimethylanilinium-oxide on direct insertion into the ionization chamber appears to evaporate without any structural rearrangement despite the fact that it cannot become covalent by electronic rearrangements through conjugation. The *meta* and *para* analogues underwent structural changes.⁸ For comparison the *ortho* isomers of anthranilic and sulphanilic acid were diazotized and studied in the mass spectrometer. Neither the spectrum of diazotized anthranilic acid, nor the diazonium sulphionate, however, showed peaks corresponding to the zwitterions. The most important pyrolytic reaction of the hydrochloride of the diazonium carboxylate is formation of chlorobenzoic acid. Other species are also present among which a peak at m/e 152 corresponding to biphenylene which is the base peak in the spectrum of the zwitterion.

EXPERIMENTAL

The mass spectra recorded on AEI MS-902 double focusing mass spectrometer. The source temperature was kept at 50° when running the spectra of *o*- and *p*-diazo-oxides. For the other compounds the source temperature was kept at 230°. All compounds were introduced directly into the source. The electron energy was 70 eV and ionizing current 100 μ A.

Diazotation of the aminophenols^{9,10}, *o*-anthranilic acid¹¹ and *o*-sulphanilic acid¹² was performed as described in the literature.

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