89

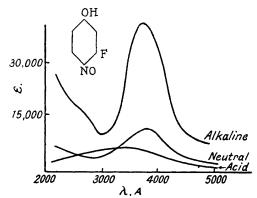
32. The Tautomerism of Benzoquinone-p-Nitrosophenol Systems. Part II. 3-Fluoro-4-nitrosophenol.

By HERBERT H. HODGSON.

Previous work on the ultra-violet absorption spectra of the 3-halogeno-4-nitrosophenols and their isomeric oximes is now completed by the study of the absorption spectrum of 3-fluoro-4-nitrosophenol. This spectrum has unique features in accord with the experimental observation that this phenol, unlike its analogues, is not directly convertible into a quinonoid isomeride.

A STUDY of the ultra-violet absorption spectra of 3-chloro-, 3-bromo-, and 3-iodo-4-nitrosophenols had indicated (Hodgson, J., 1937, 520) that in neutral alcoholic solution there were two bands with peaks at ca. 4000 and

3000 A., corresponding respectively to the ion and the unionised compound. The former band was eliminated by acids, and the latter by alkalis. Similar bands with peaks at ca. 4000 and 3000 A. were obtained for the corresponding 3-halogeno-4benzoquinoneoximes, which were also eliminated by acids and alkalis respectively. It has been found, however (Hodgson and Nicholson, J., 1940, 1268), that 3-fluoro-4-nitrosophenol is incapable of conversion into the isomeric (unknown) 3-fluorobenzoquinone-4-oxime, and as a result it is exceedingly stable; e.g., it is precipitated unchanged by acids from alkaline solutions, whereas the analogues are all converted by alkalis into the isomeric oximes; it has m. p. 161°, about mid-way between the m. p.'s of the nitroso- and the quinoneoxime forms of the analogues, does not form a picrate (cf. Hodgson, J., 1931, 1494), and is unattacked by diazomethane (cf. Hodgson, J., 1932, 1395). Moreover, the deep green colour of 3-fluoro-4-nitrosophenol, its mode of formation either by direct nitrosation or by demethylation of 3-fluoro-4-nitroso-anisole, and



Absorption spectra of 3-fluoro-4-nitrosophenol in acid, neutral, and alkaline solution.

the failure to form a silver salt (cf. Hodgson, *loc. cit.*), all indicate a nitroso-structure. In addition, stability and relatively high m. p. are evidence of considerable polarisation [cf. Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," 1932, p. 22].

The absorption spectrum (see fig.) of 3-fluoro-4-nitrosophenol possesses unique features in accord with the foregoing properties. There is only one band, with peak at 3700 A. (i.e., between the ionised and the un-ionised

bands of the analogues), and although this band happens to be in the vicinity of the single bands given by the 3-halogeno-4-nitrosoanisoles, it is eliminated by acids and intensified by alkalis, and corresponds, therefore, to the anion. The un-ionised substance apparently absorbs very little within the wave-length range (2200—5000 A.) investigated, and at the concentration employed (3.2×10^{-4} N).

The large displacement (ca. 300 A.) of the band towards the shorter wave-lengths, compared with the positions of the ionic bands of the analogues, indicates that relatively the electronic strain is much greater in the 3-fluoro-4-nitroso-anion, and it is suggested that the cause arises from a partial betaine (dipolar) structure

 $\stackrel{\theta}{H}\stackrel{\theta}{O}\rightarrow \stackrel{\bullet}{\longrightarrow} \stackrel{\delta-\delta+}{\stackrel{\delta-\delta+}{\longrightarrow}} \stackrel{\bullet}{N}$

of the anion (see inset), which effects almost complete closure of the external electrical field by what is virtually 5-membered-ring formation. In such a dipolar condition of the anion, the N-oxygen atom is prevented from becoming anionoid, and so is incapable of combination with a hydrogen ion. The nitroso-structure of the 3-fluoro-4-nitroso-anion is thus essentially preserved, whereas by contrast the nitroso-structures of the analogous anions are very unstable and readily pass over into stable

quinoneoxime forms which will not revert to the original nitroso-structures.

Note. In Part I (J., 1937, 52) line 8 should read: "the 3-halogenobenzoquinone-4-oximes could not be converted directly into the isomeric nitrosophenols" (instead of oximes as printed).

Experimental.—All measurements were made by means of a Hilger ultra-violet Spekker Spectrophotometer, the absorption due to a 1, 2, or 4 cm. path of solution being compared photographically with that of a blank cell filled with the solvent used. The 3-fluoro-4-nitrosophenol was dissolved in water containing a trace of alcohol at a concentration of 46.8 mg./l., i.e., $3.2 \times 10^{-4} \text{ N}$. The pH values of the neutral, acid, and alkaline solutions were respectively 7.00, 3.24, and 10.42 as measured on a standard Cambridge pH meter.

The author gratefully acknowledges his indebtedness to Dr. H. Lowery, Principal of the South-West Essex Technical College and School of Art, and to his Research Assistant, Mr. D. Price, B.Sc., for measurement of the spectra.

TECHNICAL COLLEGE, HUDDERSFIELD.

[Received, January 7th, 1943.]