

117. *The Tautomerism of Benzoquinoneoxime-p-Nitrosophenol Systems.*

By HERBERT H. HODGSON.

ALTHOUGH *p*-nitrosophenol and *p*-benzoquinoneoxime are prepared respectively by the action of nitrous acid on phenol and by the condensation of hydroxylamine with *p*-benzoquinone, yet the product in each case is represented by the tautomeric equilibrium $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO} \rightleftharpoons \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NOH}$. From a spectroscopic study of this tautomerism, Baly, Edwards, and Stewart (J., 1906, **89**, 520) concluded that in neutral environment the nitroso-structure prevailed, whereas in alkaline solution the salt was in the quinoneoxime form. A like conclusion was reached by Hodgson and his collaborators (J., 1925, **127**, 2260; 1929, 1555; 1932, 1395) from the low melting point of *p*-nitrosophenol and its ability to react with diazomethane to give glyoxime *NN'*-di-4-methoxyphenyl ether. The diametrically opposite conclusion was drawn by Anderson and Geiger (J. Amer. Chem. Soc., 1932, **54**, 3064), who argued that the absorption spectrum of each of the tautomerides, if it could be obtained pure, would be similar to that of its methyl ether, and since the methyl ethers do not undergo tautomerism under the conditions employed, a comparison of the spectra should aid the determination of the ratio of the tautomerides in the equilibrium mixture. The results of Anderson and Geiger were claimed to be confirmed by Anderson and Yanke (*ibid.*, 1934, **56**, 732) for the forms existing in the following solvents: ether, dioxan, chloroform, absolute alcohol, and aqueous acids; the experiments were also extended to measurements of the absorption spectra of 3-chloro-4-nitrosophenol, 3-chlorobenzoquinone-4-oxime, and their respective methyl ethers.

Anderson and Yanke (*loc. cit.*) found that the absorption spectrum of 3-chlorobenzoquinone-4-oxime was very similar to that of its methyl ether, but, most peculiarly, that of 3-chloro-4-nitrosophenol was unlike both that of its ether and that of its isomeric quinonoid modification. Since these authors could not ascribe such differences either to ionisation or to association of the nitrosophenolic form, for conductivity measurements indicated that the so-called tautomerides were dissociated to the same extent, they cited the work of Hantzsch (*Ber.*, 1917, **50**, 1422) on dissociable acids to resolve their dilemma, and stated that whatever the fundamental cause might be, it was probably explicable in the same terms for each group of compounds. Finally, Anderson and Yanke (*loc. cit.*) concluded that 2-chloro-4-nitrosophenol also existed mainly in the quinonoid modification because of the similarity between its absorption spectrum and that of 2-chlorobenzoquinone-4-

oxime methyl ether, notwithstanding the author's opposite conclusion (J., 1932, 866) based on incontrovertible chemical data.

The author and his collaborators have shown, and it has been confirmed by Anderson and Yanke, (i) that the 3-halogeno-4-nitrosophenols and the isomeric oximes are unimolecular in alcohol, benzene, chloroform, dioxan (pure and aqueous solutions), ether, naphthalene, phenol, and aqueous acids, and (ii) that, under all the experimental conditions as yet tried (including those of Anderson and his collaborators), the 3-halogenobenzoquinone-4-oximes could not be converted directly into the isomeric oximes, whereas the latter are rapidly transformed by alkalis into the former and more slowly by concentrated acids. In view of these facts, the conclusions of Anderson and his collaborators would appear to be premature and in some cases erroneous.

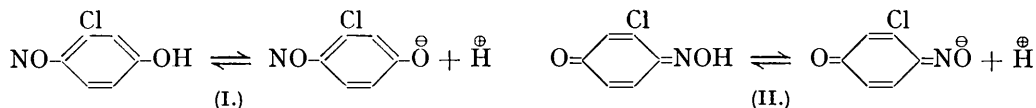
In order to support the chemical results by physical data, the absorption spectra of the 3-chloro-, 3-bromo-, and 3-iodo-4-nitrosophenols and of the corresponding isomeric oximes have now been measured in neutral, acid, and alkaline solutions. A similar study has also been made of 2-chloro-4-nitrosophenol, which, as judged by chemical data, exists only in the quinonoid modification in its salts and not in the free state. For comparison purposes, the absorption spectra of the methyl ethers of the above eight compounds have also been measured, together with those of *p*-nitrosophenol, *p*-nitrosoanisole, and *p*-benzoquinoneoxime methyl ether.

All the measurements now recorded were carried out with equivalent solutions of the several compounds in what was practically an aqueous medium, a condition which enabled ionisation (if any) to be freely developed, although Anderson and Yanke (*loc. cit.*), using dioxan-water mixtures as solvent, found that there was only a slight change in the absorption spectra during wide variations of the solvent composition. The resulting data are claimed to confirm the author's earlier conclusions based on purely chemical data, and also to resolve some of the difficulties abandoned by Anderson and his collaborators.

Apparatus.—The measurements were made with a polarisation type of spectrophotometer, the spectrograph being the Bellingham-Stanley Model No. 2, with quartz optical system of dispersion such that the spectrum from 2100 to 8000 Å. was obtained on a single 10" plate. The light source employed was the arc between iron electrodes in air. All the compounds were measured at the same molecular concentration in aqueous solutions containing but a trace of alcohol, and at a dilution of the order $4 \times 10^{-4}N$.

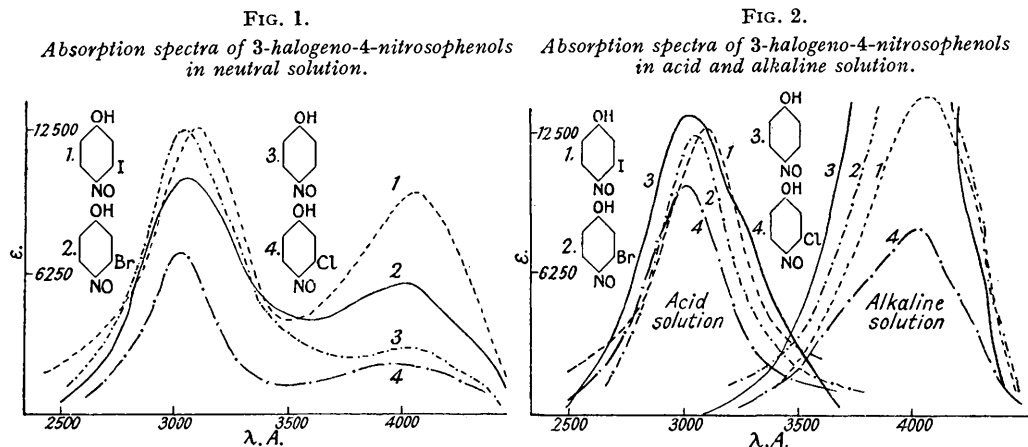
Discussion of the Absorption Spectra with Respect to the Chemical Constitution of the Compounds.

Since 3-chloro-4-nitrosophenol is a chemical individual which is obtained by the action of nitrous acid on *m*-chlorophenol (Hodgson and Moore, J., 1923, 123, 2499) and crystallises unchanged from neutral solvents, including aqueous alcohol, with no evidence of its association, it is obvious that in neutral aqueous-alcoholic solution there should be present three entities, *viz.*, the un-ionised substance, its anion, and the hydrogen ion (I). The absorption spectrum (Fig. 1) confirms this anticipation, there being two very definite bands with peaks at 4010 and 2990 Å.; these bands are eliminated respectively by excess of acid and of alkali (Fig. 2), and must therefore correspond respectively to the anion and the un-ionised 3-chloro-4-nitrosophenol. Similarly, 3-chlorobenzoquinone-4-oxime also must exist in neutral aqueous-alcoholic solution as an equilibrium between un-ionised substance and its ions (II), for the two absorption bands with peaks at 3030 and 3990 Å. (Fig. 3) are eliminated respectively by excess of alkali and excess of acid (Fig. 4).

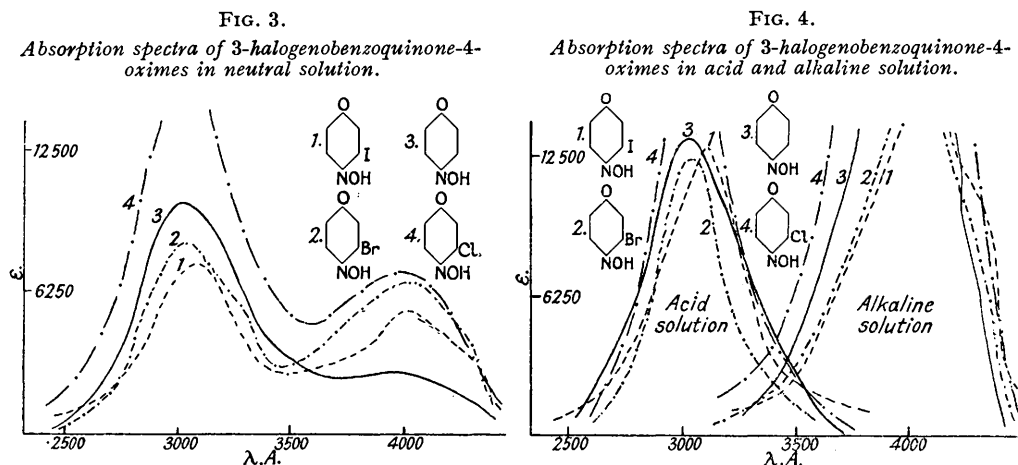


The apparent approximate identity of the above absorption spectra (compare Figs. 1 and 3) might lead to the premature conclusion that the substances were identical in solution, but such a deduction must be erroneous, since both substances separate unchanged

from aqueous alcohol, in which, incidentally, the quinoneoxime is far more soluble than the nitrosophenol. Furthermore, if tautomeric equilibrium were established on dissolution, then on subsequent crystallisation the solutions of both forms should afford the nitroso-form in the first separations, whereas the initial substance separates in a pure condition in each case. When, however, a mixture of 3-halogeno-4-nitrosophenol and the corresponding oxime is recrystallised from aqueous alcohol, it is the nitroso-form that



separates first. Moreover, 3-chloro-4-nitrosophenol is exceedingly sensitive to reagents, and the 3-bromo- and the 3-iodo-analogue still more so, and all attempts to cause reaction with the phenolic hydrogen (Hodgson, J., 1931, 1494) have resulted in conversion either into the quinoneoxime form itself or into that reaction product which the quinoneoxime affords under identical conditions. For example, both isomerides give the same silver salt, which on treatment with methyl iodide yields the 3-halogenobenzoquinone-4-oxime



methyl ether, a product also produced from the 3-halogeno-4-nitrosophenols by reaction with methyl sulphate and alkali and with ethereal diazomethane. Both isomerides (previously styled tautomerides) react with *p*-nitrophenylhydrazine to give the same *p*-nitrophenylhydrazone; further, dry hydrogen chloride rapidly converts the nitrosophenols into quinoneoximes in ethereal solution, and aluminium chloride and hydrogen chloride react vigorously with the 3-halogeno-4-nitrosoanisoles in dry ether to give the 3-halogenobenzoquinone-4-oximes. On the other hand, the 3-halogeno-4-nitrosophenols readily

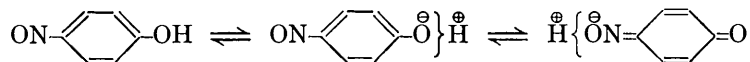
form unimolecular picrates, whereas the quinoneoximes do not, and diazomethane reacts with true nitroso-compounds to form derivatives of glyoxime, whereas quinoneoximes give rise to their methyl ethers.

Differences in the absorption spectra of these isomeric nitrosophenols and quinoneoximes should therefore be sought in the bands of the respective un-ionised compounds and of their anions identified as above, and such differences are found in the respective molecular extinction coefficients (ϵ), which vary markedly between the different compounds.

Anderson and Yanke (*loc. cit.*) found that the absorption spectra of their so-called quinoneoximes were very sensitive to changes in hydrogen-ion concentration between p_H 3 and p_H 7, and independent of these factors at p_H values outside this range. Such variations would naturally be expected, since changes of ionisation of the products in the weakly acid medium ($p_H > 3$) would be accompanied by pronounced changes in the densities of absorption, whereas in strongly acid medium ($p_H < 3$), the un-ionised product would alone exist and absorption would become constant so far as this product was concerned. Similarly, in an alkaline medium ($p_H > 7$), the un-ionised substance ceases to exist, and with complete ionisation the absorption becomes practically stabilised.

The two bands for 3-chloro-4-nitrosophenol have $\epsilon = 6875$ and 1875 for 2990 A. and 4010 A. respectively, whereas the two bands of 3-chlorobenzoquinone-4-oxime have $\epsilon = 15,000$ for 3030 A. and $\epsilon = 6875$ for 3990 A., indicating that very probably four distinct entities are being measured, *viz.*, the two un-ionised compounds and their respective ions; in presence of excess hydrochloric acid, which represses ionisation, the values of ϵ for the single bands of the un-ionised 3-chloro-4-nitrosophenol and of 3-chlorobenzoquinone-4-oxime become 8750 and 17,500 respectively, showing a small increase due to elimination of the ions. The ϵ 's of the single bands of 3-chloro-4-nitrosoanisole and of 3-chlorobenzoquinone-4-oxime methyl ether are 10,625 for 3625 A. and 14,375 for 3180 A., and throughout the series the values of ϵ for the ethers are of the same order of magnitude as the values for the un-ionised hydroxylic compounds, the smaller ϵ 's corresponding to the molecules under the greater electronic strain.

Similarly *p*-nitrosophenol itself exhibits two bands with peaks at 3020 and 3965 A. (Fig. 1), the former being suppressed by alkalis and the latter by acids (Fig. 2), and they therefore correspond to the un-ionised compound and an anion which perhaps in this case is in equilibrium with its tautomeric ion:



The chemical evidence, however, indicates that *p*-nitrosophenol in ethereal solution is mainly in the nitroso-form, since diazomethane converts it almost entirely into a glyoxime derivative (Hodgson, J., 1932, 1395), whilst the low m. p. of the solid, which is in the vicinity of the m. p.'s of the true 3-halogeno-4-nitrosophenols, points to the nitroso-structure in the crystalline state.

The above phenomena are repeated (see Figs. 1 and 3, and table) in the cases of 3-bromo- and 3-iodo-4-nitrosophenols and of the corresponding oximes. Whereas, however, the absorption curves for 3-chloro-4-nitrosophenol and its oxime form in acid and in alkaline solution indicate a considerable stability (retarded conversion for the nitroso-form), the corresponding curves for the bromo- and the iodo-analogue (Figs. 5 and 6) indicate that immediate conversion of both 3-bromo- and 3-iodo-4-nitrosophenol into the more stable quinoneoximes has taken place in both the acid and the alkaline environment. These facts support the chemical facts that 3-bromo- and 3-iodo-4-nitrosophenols are exceedingly sensitive to reagents and even to solvents (Hodgson and Moore, J., 1925, 127, 2260).

The 3-halogeno-4-nitrosoanisoles (Fig. 7) exhibit very similar single absorption bands with their peaks at about 3625 A., *i.e.*, between the bands of the un-ionised and the ionic forms of the corresponding non-methylated compounds. The relative molecular extinction coefficients of these bands are of the same order, and all but one are less than that of the non-halogenated *p*-nitrosoanisole, which has its peak at 3500 A. and $\epsilon = 13,750$. Any other minor peaks in the absorption spectra are probably due to the presence of un-

methylated compound arising from the incipient decomposition which sets in on keeping and results eventually in the complete conversion of the 3-halogeno-4-nitrosoanisole into the corresponding benzoquinone-4-oxime.

The methyl ethers of the 3-halogenobenzoquinone-4-oximes similarly possess single absorption bands (Fig. 8) with peaks at *ca.* 3200 Å. and ϵ 's *ca.* 12,000; *p*-benzoquinone-oxime methyl ether has its band very similarly situated to that of the 3-bromo-analogue.

FIG. 5.

Comparison of absorption spectra of 3-iodo-4-nitrosophenol and 3-iodobenzoquinone-4-oxime in neutral solution.

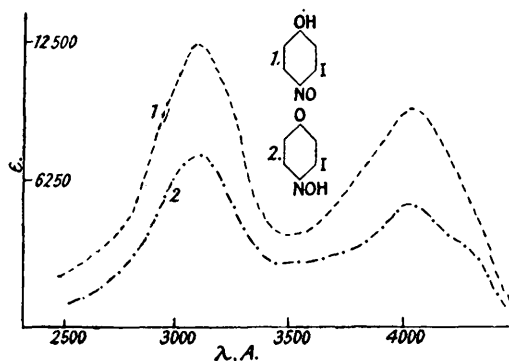
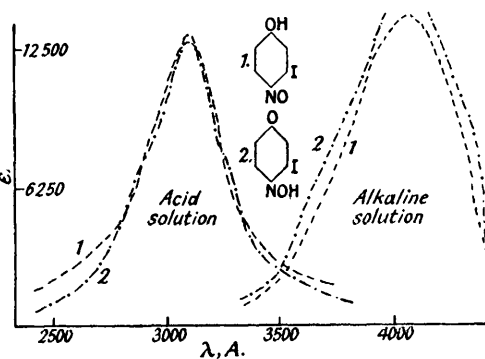


FIG. 6.

Comparison of the absorption spectra of 3-iodo-4-nitrosophenol and 3-iodobenzoquinone-4-oxime in acid and alkaline solution.



It will be obvious, therefore, that it may be highly fallacious to base conclusions as to the tautomeric form in which the substituted nitrosophenols and quinoneoximes exist on a mere comparison of their absorption bands with those of their respective methyl ethers. Further, Baker and Nathan (J., 1935, 1840) have pointed out that a special reaction mechanism must be assigned to the methyl group when attached to a conjugated system which differentiates it from the other alkyl groups, and the present author suggests

FIG. 7.

Absorption spectra of 3-halogeno-4-nitrosoanisoles.

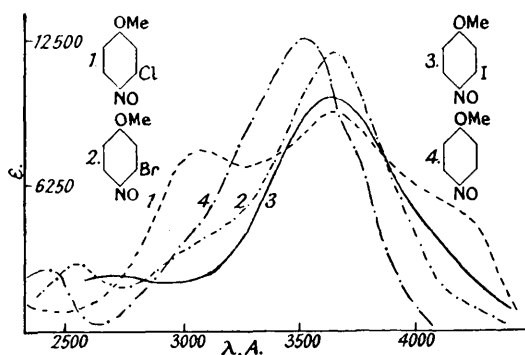
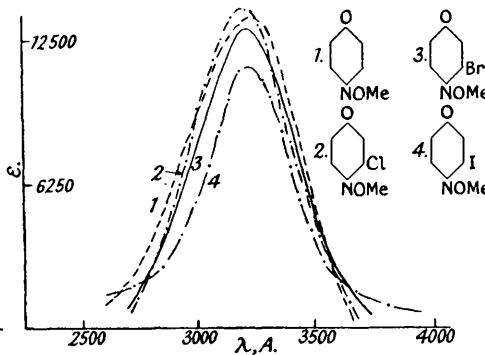


FIG. 8.

Absorption spectra of the 3-halogenobenzoquinone-4-oxime methyl ethers.



that such a possible rôle in other states of combination may vitiate any conclusions such as those which Anderson and his collaborators have drawn (cf. Ingold, *Chem. and Ind.*, 1936, 963). Likewise, on Anderson's argument, the bands of the methyl ethers on such a comparison basis should correspond with those ascribed to the un-ionised compounds, and the accompanying table should completely reveal such a fallacy.

It will be noticed that the peak for nitrosobenzene itself occurs in the vicinity of those for the un-ionised compounds, thereby indicating that the nitroso- and the oximino-group are the prime centres of activity so far as absorption is concerned; that its wave-

TABLE.

(The molecular extinction coefficients, ϵ , corresponding to the various peaks are the mean values over all the measurements made.)

Compound.	Band due to ion.		Band due to un-ionised compound.		Band of methyl ether.	
	Peak (A.).	ϵ .	Peak (A.).	ϵ .	Peak (A.).	ϵ .
3-Chloro-4-nitrosophenol	4010	1875	2990	6,875	3625	10,625
3-Bromo-4-nitrosophenol	4015	5625	3040	12,500	3620	11,875
3-Iodo-4-nitrosophenol	4050	9375	3080	12,500	3625	10,940
3-Chlorobenzoquinone-4-oxime ...	3990	6875	3030	15,000	3180	14,375
3-Bromobenzoquinone-4-oxime ...	4015	6250	3040	8,750	3200	13,125
3-Iodobenzoquinone-4-oxime	4030	5625	3080	7,500	3200	11,250
<i>p</i> -Nitrosophenol	3965	2500	3020	9,375	3500	13,750
<i>p</i> -Benzoquinoneoxime						
Nitrosobenzene	—	—	3160	—	—	—

length exceeds that of any un-ionised hydroxyl compound shows the greatest relief from electronic strain in the unsubstituted compound.

FIG. 9.

Absorption spectra of 2-chloro-4-nitrosophenol in neutral and acid solution.

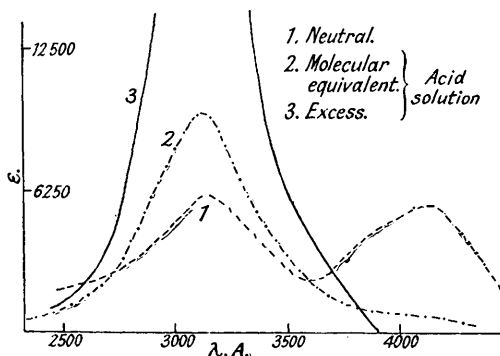
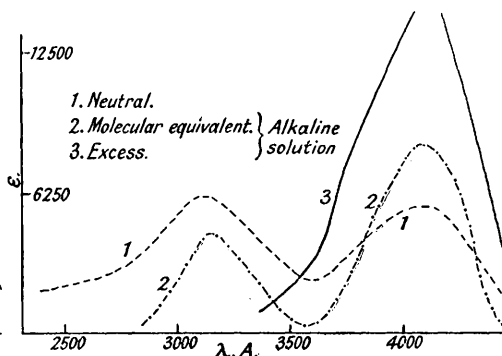


FIG. 10.

Absorption spectra of 2-chloro-4-nitrosophenol in neutral and alkaline solution.



Although Anderson and Yanke's experimental results are apparently confirmed in so far as the peaks of the bands of the quinone methyl ethers are nearer to those of the un-ionised compounds than are the corresponding peaks of the nitrosoanisoles, yet there is not even approximate identity between the bands themselves, and the differences can hardly be ascribed to the mere replacement of hydrogen by the methyl group, the system being far too complex for the toleration of such a conclusion. It will be noticed, however, that the bands of the methyl ethers have peaks in all cases at longer wave-lengths than those of the un-ionised compounds, whether of nitrosophenols or of quinoneoximes, and that this displacement conforms to the requirements of modern electronic theory, since the inductive electron-repelling (+I) effect of the methyl group is greater than that of covalently bound hydrogen. On the other hand, the anions, in all cases, absorb at the longest wave-lengths, in conformity with the fact that they possess a free negative charge; since this charge must predominate over all other partial effects, the ionic absorption is found to be practically the same for most of the compounds.

The great disparity between the positions of the absorption bands for the un-ionised 3-halogeno-4-nitrosophenols and for the corresponding anisoles (of the order of 600 Å.) can be accounted for by the much greater electronic strain in the phenols, resulting ultimately in ionisation, and, since the anticipated order of strain would be Cl > Br > I, this is confirmed by corresponding displacements of the bands both for the ionised and for the un-ionised parts of the dissociation equilibrium towards the longer wave-lengths in the order, Cl < Br < I, i.e., corresponding to the order of strain. The 3-halogenobenzoquinone-4-oximes, on the other hand, are the more stable isomerides and incapable of

conversion into the nitroso-forms, so that the effects of groups are much less pronounced (the peak separation is of the order 150 A.) than in their much less stable nitroso-isomerides where the tendency (mesomeric) is towards conversion.

Anderson and Yanke (*loc. cit.*) dismiss the case of 2-chloro-4-nitrosophenol in one paragraph, in which they state that Hodgson concluded that the product existed in the benzenoid form from the simple fact of its low melting point. Anderson and Yanke ignore the other evidence which Hodgson accumulated in favour of his verdict, *viz.*, formation of a picrate, probable co-ordination between the chlorine atom and the hydroxyl group (cf. Sidgwick and Callow, J., 1924, **125**, 533), the recrystallisation of the compound unchanged from ether saturated with hydrogen chloride (cf. the facile transformation of the low-melting 3-chloro-isomeride into the much-higher-melting 3-chlorobenzoquinone-4-oxime), its precipitation unchanged from solutions in alkaline hydroxides and alkaline carbonates by mineral acids, and the significant facts that the quinoneoxime modification has only hitherto been found in its salts, in a methyl ether, and in condensation products with *p*-nitrophenylhydrazine and semicarbazide. Further, a subsequent publication by Hodgson (J., 1932, 1395) has been completely overlooked, in which diazomethane was reported as reacting with 2-chloro-4-nitrosophenol to form glyoxime *NN'*-di-3-chloro-4-methoxyphenyl ether and 2-chlorobenzoquinone-4-oxime methyl ether in approximately

FIG. 11.

Comparison of absorption spectra of 2-chloro- and 3-chloro-nitrosophenols in neutral solution.

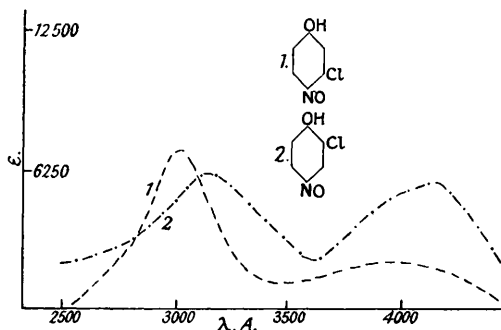
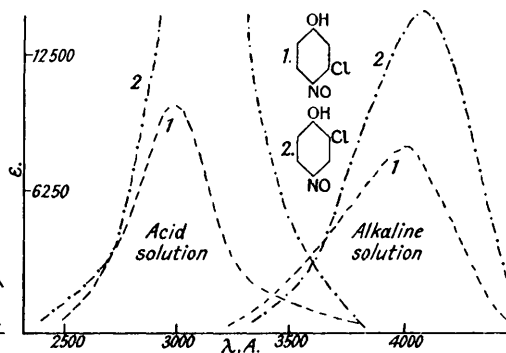


FIG. 12.

Comparison of absorption spectra of 2-chloro- and 3-chloro-4-nitrosophenols in acid and alkaline solution.



equal amounts. Now, diazomethane itself converts nitrosophenols into quinoneoximes and never effects the reverse process, so the quinoneoxime ether above is undoubtedly the result of partial isomerisation produced by the diazomethane, whereas sufficient retardation has been exerted by the tendency to chelation between hydroxyl and chlorine to favour the preservation of the nitroso-form in some molecules (about half the number) and their subsequent conversion into the glyoxime product.

The absorption spectrum of 2-chloro- is very similar to that of 3-chloro-4-nitrosophenol (Fig. 11) with two bands having peaks at 3125 A. ($\epsilon = 6250$) and 4125 A. ($\epsilon = 5625$) respectively, the band of longer wave-length being suppressed by acids and the other by alkalis (Fig. 10), and therefore corresponding to the anion and the un-ionised compound. Both bands are at longer wave-lengths than the corresponding pair of 3-chloro-4-nitrosophenol (2990 and 4010 A.), indicating that the electronic strain in the 2-chloro-compound is less than that in its 3-chloro-isomeride. The peak of the band given by 2-chloro-4-nitrosophenol is at 3500 A., and that of 2-chlorobenzoquinone-4-oxime methyl ether at 3300 A. (Fig. 13), *i.e.*, nowhere near the peaks of 2-chloro-4-nitrosophenol itself (Figs. 9 and 10), so that, despite Anderson and Yanke's conclusion, based on their fallacious comparison of the ethers with the free phenol, it must be obvious that the product is in the benzenoid form. The low melting point rule of Hodgson and Moore (J., 1925, **127**, 2260), *viz.*, that "nitroso-compounds melt at a lower temperature than the isomeric quinoneoximes," is thus obeyed, and no exceptions to the rule have yet been recorded. It was the above

rule which led to a comprehensive investigation of 2-chloro-4-nitrosophenol, and the evidence was more detailed than is implied by Anderson and Yanke's simple statement (*loc. cit.*, p. 733) that "Hodgson . . . because of its low melting point, believes that it existed in the benzenoid form only."

It must also be pointed out that the data for *p*-nitrosophenol, *p*-nitrosoanisole, and *p*-benzoquinoneoxime methyl ether (see table and figures) are entirely in accord with the corresponding data for the substituted derivatives.

A trial, carried out in order to determine whether recrystallisation of 3-chloro-4-nitrosophenol from alcohol had any effect on the absorption spectrum, indicated no essential change, and thereby established conclusively that this substance retained its nitroso-structure after dissolution in hot alcohol.

In the case of the measurements made in acid solution, separate data were obtained for hydrochloric and acetic acids, and both potassium hydroxide and sodium carbonate were used for the measurements in alkaline solution. This procedure provided a check, in addition to testing the possibility of different effects afforded by the highly and moderately ionised reagents. The fact that no appreciable variations were recorded, indicated that the ionisation was fully developed in each case owing to the extent of dilution required for the absorption measurements.

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