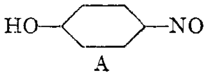
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Tautomerism of Quinoneoxime-para-nitrosophenol Systems[1]

BY LEIGH C. ANDERSON AND R. L. YANKE

Absorption spectra data which have been published from this Laboratory[2] indicated that the equilibrium mixture of *p*-nitrosophenol, A, and quinoneoxime, B, exists in ether solution largely in the quinonoid form.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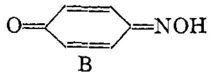
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This conclusion was based, first, on the assumption that the absorption spectrum of each of the two mentioned compounds, if it could be obtained pure, would be similar to its methyl ether, and, second, upon the fact that the absorption spectrum curve of an ether solution of the equilibrium mixture is very similar to the curve for the methyl ether of quinoneoxime and different from the curve for the methyl ether of the benzenoid form, *p*-nitrosoanisole.

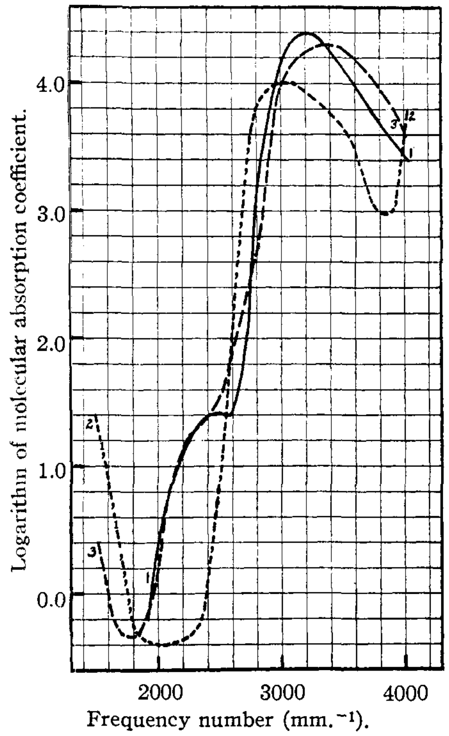

Fig. 1.—Dioxane solutions of: 1, quinoneoxime methyl ether; 2, *p*-nitrosoanisole; 3, tautomeric mixture of quinoneoxime and *p*-nitrosophenol.

Quinoneoxime-para-nitrosophenol Systems in Organic Solvents.—The data presented in this paper confirm our conclusion that the quinonoid modification is present to a greater extent than the benzenoid form in solutions of *p*-nitrosophenol-quinoneoxime. The curves for the quantitative absorption spectra of quinoneoxime, its methyl ether and *p*-nitrosoanisole when each is dissolved in dioxane are presented in Fig. 1. The similarity of the curves for the two former compounds is at once apparent and predicates the quinonoid structure for dioxane solutions of the hydroxyl compound. Similar conclusions can be drawn from curves that have been obtained when using chloroform and absolute alcohol solutions of the substances.

In the case of ether and dioxane solutions of 3-chloroquinone-4-oxime,[3] we have found that the assumption made in the previous work is substantiated inasmuch as the absorption curve for this substance is very similar to that of its methyl ether. The isomeric 3-chloro-4-nitrosophenol, however, possesses an absorption curve which is not similar to that of its isomer or to the curve of either of the methyl ethers. These facts are shown in Fig. 2 which presents the curves for the quantitative absorption spectra of ether solutions of these four compounds. The curves for dioxane solutions were found to be almost identical with those for the corresponding ether solutions and are not being included. The similarity of the curves for solutions of the *p*-nitrosophenol-quinoneoxime system with the curves for corresponding solutions of 3-chloroquinone-4-oxime further confirms our conclusion that in the former system, the quinonoid form predominates.

The difference in the absorption spectrum of the benzenoid form from that of its methyl ether cannot be assigned to ionization of the former compound because conductivity measurements show that the two tautomeric compounds are dissociated to about the same extent. If ionization

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(1) The material in this paper comprises a portion of a thesis presented by Robert L. Yanke to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1933.

(2) Anderson and Geiger, THIS JOURNAL, **54**, 3064 (1932).

(3) This compound and its benzenoid isomer, 3-chloro-4-nitrosophenol, together with the methyl ethers of each were described by Hodgson and Moore, *J. Chem. Soc.*, **123**, 2499 (1923), and Hodgson and Kershaw, *ibid.*, 1553 (1929).

were the cause of the dissimilarity in the case of the benzenoid form and its ether then the absorption spectrum of the quinonoid form should also be different from that of its ether; it has been pointed out, however, that such is not the case. The specific conductances (each × 10^{-6}) of 0.0075 molar solutions of these compounds when dissolved in a mixture of dioxane and water (50.6% dioxane) are as follows: 3-chloro-4-nitrosoanisole, 2.7; 3-chloroquinone-4-oxime methyl ether, 2.7; 3-chloro-4-nitrosophenol, 6.7; 3-chloroquinone 4-oxime, 6.6; benzoic acid, 8.3; and the solvent, 2.6. These values are indicative of the relative degree of ionization of the solutes since solutions of equivalent concentration were used in all cases. As might be expected, the two methyl ethers are not electrolytes and the two hydroxyl compounds have conductances that are equal to each other, within experimental error, and between the value for the ethers and that for benzoic acid. When these compounds and quinoneoxime and the sodium salt of quinoneoxime were dissolved in absolute alcohol there were obtained the following values (each × 10^{-7}): 3-chloro-4-nitrosoanisole, 2.4; the methyl ether of 3-chloroquinone-4-oxime, 2.4; 3-chloro-4-nitrosophenol, 6.2; 3-chloroquinone-4-oxime, 7.2; quinoneoxime, 5.3; sodium salt of quinoneoxime, 2200; and the solvent 2.4. The high conductance of the sodium salt when compared to the low values for the hydroxyl compounds indicates that the former is very highly ionized and the latter only slightly. Each of the forms when dissolved in ether exists in the monomolecular state, as we have found from ebullioscopic data, and therefore the unexplained difference in absorption cannot be due to association of the phenolic nitroso compound. The effect that we have noted in the case of the benzenoid isomer is apparently similar to that which Hantzsch[4] has discussed in his work on "dissociable" acids and whatever the fundamental cause may be, it is probably explainable in the same terms for each of these groups of compounds.

Hodgson[5] has reported studies on 2-chloro-4-nitrosophenol and, because of its low melting point, believes that it existed in the benzenoid form only. We find, however, that the absorption spectrum of this compound agrees very closely with those of the methyl ethers of the quinone oximes rather than the nitrosoanisoles and we conclude that like the unsubstituted quinoneoxime, it probably exists largely as the quinonoid modification.

Quinoneoxime-para-nitrosophenol Systems in Aqueous Solutions.—In order to compare the absorption spectra of aqueous solutions of the tautomeric compounds and their salts with those of the ethers, which are not soluble in water, it was necessary to find a solvent high in water content in which all of these substances would be soluble. A mixture of dioxane and water containing 94% water constitutes such a solvent. A change of the solvent from one high in dioxane content to one high in water content produces in most cases only a slight change in the absorption spectra of the compounds. The most interesting change occurs in the case of the two methyl ethers of the quinoneoximes, and is illustrated by the absorption curves in Fig. 3. As the water content increases, the absorption band near the edge of the visible shifts toward the ultraviolet and the base of the band having its peak at about 3200 mm.$^{-1}$ is moved toward the visible until finally only one intense band is found. Similar

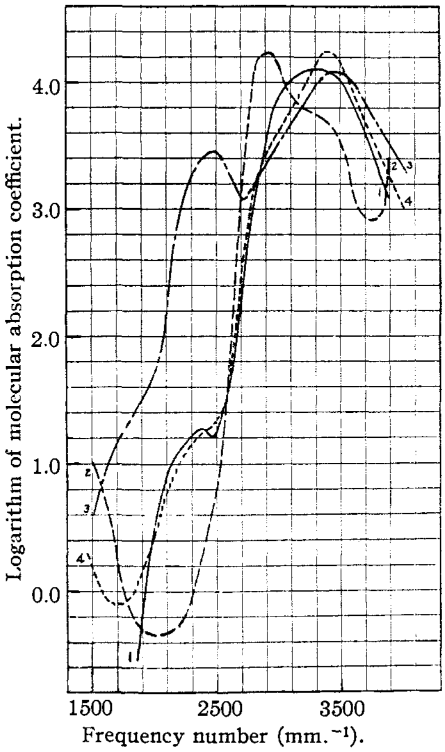

Fig. 2.—Ether solutions of: 1, 3-chloroquinone-4-oxime methyl ether; 2, 3-chloro-4-nitrosoanisole; 3, 3-chloro-4-nitrosophenol; 4, 3-chloroquinone-4-oxime.

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(4) Hantzsch, *Ber.*, **50**, 1422 (1917).

(5) Hodgson, *J. Chem. Soc.*, 866 (1932).

changes were found in the case of the methyl ether of 3-chloroquinone-4-oxime. This transition in the shape of the curve for these quinonoid compounds on changing the solvent is identical with the transition noted by Anderson and Geiger in the conversion of quinone → quinonemonoxime → quinonedioxime and of quinone → quinonemonochlorimine → quinonedichlorodiimine.

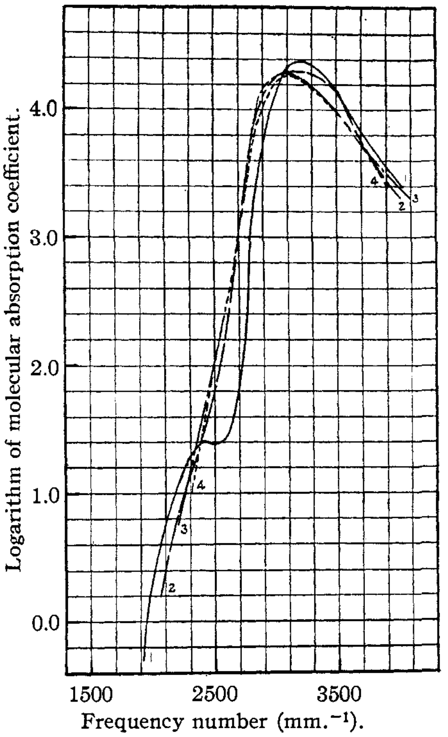


Fig. 3.—Quinoneoxime methyl ether in solution in mixtures of dioxane and water having the following composition: 1, 100:0; 2, 37:63; 3, 15.5:84.5; 4, 6:94 (dioxane: water), respectively.

The same quantitative absorption curve is obtained when either of the two isomeric forms of 3-chloro-4-nitrosophenol is dissolved in aqueous acid solution and this curve (Curve 4, Fig. 4) is so similar to that of the methyl ether of 3-chloroquinone-4-oxime (Curve 2, Fig. 4) that there can be little doubt that in this solvent the quinonoid form predominates. In alkaline solutions a curve is obtained for these compounds (Curve 3, Fig. 4) which is different from any that have been discussed thus far and, as in acid media, this curve is not dependent upon which of the isomeric forms is used. An almost identical curve is obtained from alkaline solutions of quinone oxime and, furthermore, the absorption of the alkaline solution of quinoneoxime is not dependent upon the metallic hydroxide that is used, in the visible region of the spectrum the same curve being obtained from solutions of the cobaltous, nickelous, silver, ferric, sodium or potassium derivatives.

The absorption spectra of the quinoneoximes are very sensitive to changes in hydrogen-ion concentrations between *P*H 3 and 7 and are independent of this factor at *P*H values less than 3 or greater than 7. Buffered solutions were used, therefore, in much of the work. With a buffered solution of approximately *P*H 5, a curve (Curve 5, Fig. 4) was obtained for a solution of either quinoneoxime or its chloro analog that was somewhat similar to the curve (Curve 3, Fig. 2) for solutions of 3-chloro-4-nitrosophenol in either ether or dioxane. Almost this same curve was obtained when the absorption curve for the pure sodium salt was ascertained in solution in a mixture composed of dioxane and water in the ratio of 95 : 5. Conductivity measurements of solutions of the sodium salt indicated a decided

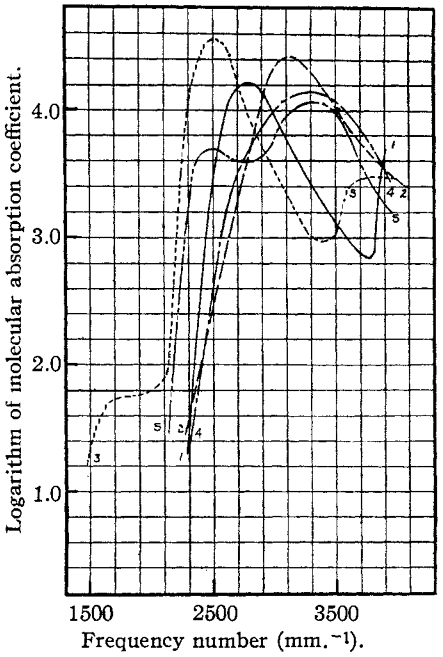
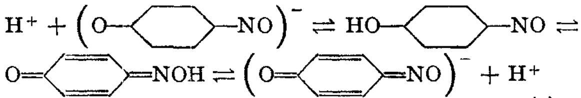


Fig. 4.—1, 3-Chloro-4-nitrosoanisole in mixture of dioxane (3.5) to water (96.5); 2, 3-chloroquinone-4-oxime methyl ether in mixture of dioxane (3.5) to water (96.5); 3, 3-chloroquinone-4-oxime and 3-chloro-4-nitrosophenol in buffer solution having *P*H 10.6; 4, 3-chloroquinone-4-oxime and 3-chloro-4-nitrosophenol in buffer solution having *P*H 0.9; 5, 3-chloro-4-nitrosophenol in buffer solution having *P*H 4.8.

decrease in ionization as the water concentration in the dioxane–water mixture used as solvent was decreased below 25%; at 5% the specific conductance was no greater than of the solvent alone. The sodium salt precipitated in mixtures of dioxane containing less than 5% of water.

If the quinonoid form predominates in acid solution, as our absorption spectra data indicate, then the above conductivity data may be used to demonstrate that the quinonoid form probably predominates in alkaline solution also. The equation indicates that the only factor that would shift the equilibrium from one form to the other



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would be a difference in the degree of ionization of the two isomeric forms. The practically equal conductances of the two forms of the chloronitrosophenols indicate that there is no marked difference in their ionization and therefore one would expect little change in the equilibrium on changing from acid to alkaline solutions. It should be noted, however, that the experimental error in determining the conductances of these solutions is rather large, due to the low solubility of the substances and high resistance of the solutions, and it is not possible to say that there is absolutely no change in the ratio of the two forms present in the two media.

The absorption spectra data were obtained by methods which have been described.[6] The compounds used in these investigations were prepared by methods which have been published and each substance was carefully purified. All solvents were optically clear within the range of the spectrum under investigation.

Summary

1. Absorption spectra data indicate that the equilibrium mixture of quinonemonoxime and *p*-nitrosophenol exists largely in the quinonoid modification in dioxane, chloroform, absolute alcohol and aqueous acid solutions.

2. The absorption spectrum of 3-chloroquinone-4-oxime is very similar to that of its methyl ether while the absorption spectrum of 3-chloro-4-nitrosophenol is unlike that of its ether or isomeric quinonoid modification. This difference is not due to ionization nor to association of the nitrosophenol form.

3. The absorption spectra of alkaline solutions of the quinoneoximes are due to a highly ionized form and it appears probable that they are also due mostly to the ion from the quinonoid modification.

(6) Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

d-Ethoxybutyl Urea[1]

BY E. WERTHEIM

In attempting to view the sweet taste of organic compounds from the standpoint which has proved successful in dealing with dyes, we may consider each compound the possessor of certain groups which have specific taste effects. In Dulcin the taste groups would be carbamido and ethoxy. These are held in a fixed position by the benzene ring. This paper reports the preparation of *d*-ethoxybutyl urea, in which the ring effect is absent but the identical groups are so held that they may assume the space arrangement found in Dulcin.[2]

The series of reactions used to prepare *d*-ethoxybutyl urea is sufficiently indicated by the following succession of formulas: $HOC_3H_6OH \longrightarrow EtOC_3H_6OH \longrightarrow EtOC_3H_6Br \longrightarrow EtOC_3H_6CN \longrightarrow EtOC_4H_8NH_2 \longrightarrow EtOC_4H_8NHCONH_2$.

The compound was found to be slightly bitter, resembling in this respect other aliphatic ureas which have been reported. It is thus established that while the relative position of the taste groups in Dulcin cannot be altered without destroying the sweetness, the ring framework must also be retained.[3] Work on the subject of taste *vs.* structure in Dulcin will be continued in this Laboratory.

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(1) Paper No. 338, Journal Series, University of Arkansas.

(2) *Cf.* previous discussion, Wertheim, THIS JOURNAL, **55**, 2540 (1933).

(3) Similarly, β-hydroxyethyl urea recently has been prepared in this Laboratory and found to be practically tasteless. *o*-Hydroxyphenyl urea, on the other hand, is very sweet.