

Summary

1. Curves have been prepared which show the quantitative absorption spectra of the methane, colored carbinol and fuchsones of each of the following compounds: 3-chloro-4-hydroxytriphenylcarbinol, 3-bromo-4-hydroxytriphenylcarbinol, 3,5-dichloro-4-hydroxytriphenylcarbinol and 3,5-dibromo-4-hydroxytriphenylcarbinol together with the curves for the colorless carbinols of the last three compounds.

2. Symmetrical or unsymmetrical substitution in the ortho positions to the nuclear hydroxyl group of 4-hydroxytriphenylcarbinol has been shown to have a definite effect upon the height of the quinonoid band for the colored carbinol; symmetrical substitution producing a greater absorption.

3. The direction of the displacement of the quinonoid band for the colored carbinol, in reference to the position for the quinonoid band for the corresponding fuchsones of the 4-hydroxytriphenylcarbinol series has also been found to be dependent upon the groups substituted in the ortho positions to the nuclear hydroxyl. If the two groups are the same the displacement is in one direction, while if they are different, the displacement is in the opposite direction.

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

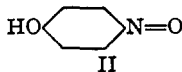
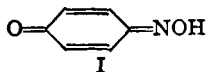
THE TAUTOMERISM OF QUINONEOXIME AND PARA-NITROSOPHENOL

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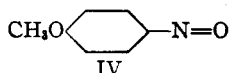
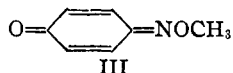
The chemical reactions and the methods of preparation of quinoneoxime (I) indicate that it is in tautomeric equilibrium with *p*-nitrosophenol (II); the relative amounts of the two substances present being dependent upon the solvent and conditions which are employed.



It has been generally accepted that the methyl ethers of tautomeric substances do not undergo tautomerization and that in many instances each can be obtained pure. A comparison of the physical properties of a solution of the tautomeric mixture of non-methylated substances with solutions of each of the corresponding methyl ether isomers has been used in investigations of compounds such as isatin, acetoacetic ester, etc., to determine the extent to which each of the tautomeric forms occurs in the equilibrium mixture. This procedure has been followed in the present investigation in the case of the mixture of quinoneoxime and *p*-nitrosophenol. Ether has been chosen as the solvent because it is optically

clear in the visible and ultraviolet regions, it is chemically inert toward solutes and also because all the compounds included in this work are monomolecular in this solvent. Sluiter¹ has shown that *p*-nitrosophenol, which is polymolecular in most solvents, is monomolecular in ether regardless of the concentration of the solution.

The methyl ethers of quinoneoxime (III) and of *p*-nitrosophenol (IV) have been described in the literature. A comparison of the quantita-



tive absorption spectrum of the tautomeric mixture of quinoneoxime and *p*-nitrosophenol with that of each of the ethers should indicate which form is present to the greater extent. These curves are presented in Fig. 1. The similarity in the curves for quinoneoxime methyl ether and the tautomeric mixture is obvious. The absorption curve for *p*-nitrosoanisole differs from the curves of the other solutions in that it shows no indication of fine bands in the edge of the visible region and the band in the ultraviolet is much narrower.

The similarity of the curves for the tautomeric mixture and quinoneoxime methyl ether leaves no doubt that the mixture in ether solution is mainly in the quinoneoxime form. On the assumption that the curves for pure quinoneoxime and pure *p*-nitrosophenol should be similar each to the curve for the corresponding methyl ether, it is possible from Fig. 1 to

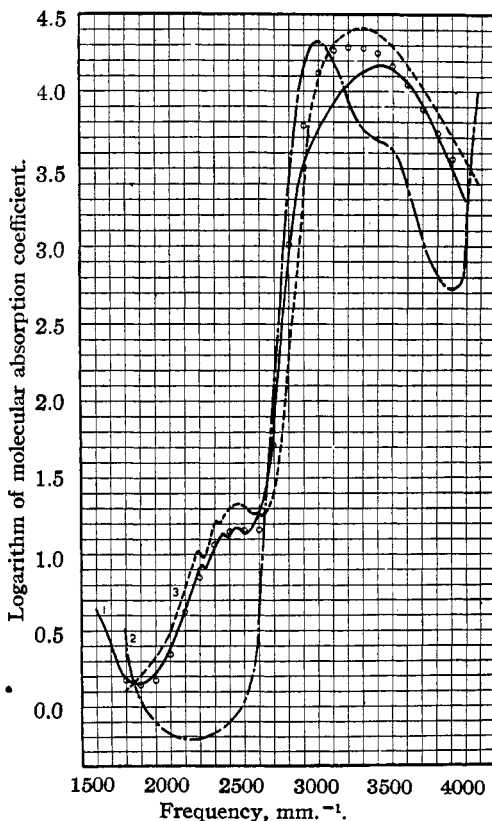


Fig. 1.—1, Tautomeric mixture of quinoneoxime and *p*-nitrosophenol; 2, *p*-nitrosoanisole; 3, quinoneoxime methyl ether.

make an estimate of the composition of the mixture. A comparison of the

¹ Sluiter, *Rec. trav. chim.*, **25**, 8 (1906).

quantitative absorption curves which are given in Fig. 2 for hydroquinone and its mono- and dimethyl ethers indicates that in these compounds the principal effect produced upon methylation is a displacement of the absorption toward the shorter wave lengths.

An examination of the curves in Fig. 1 shows that between frequencies 2000 and 2500 mm^{-1} the *p*-nitrosophenol tautomer should have little influence on the height of the curve of the mixture; and since curve 1 is about 70% as high as curve 3 within this region, the mixture should contain approximately 70% quinoxneime and 30% *p*-nitrosophenol. Using

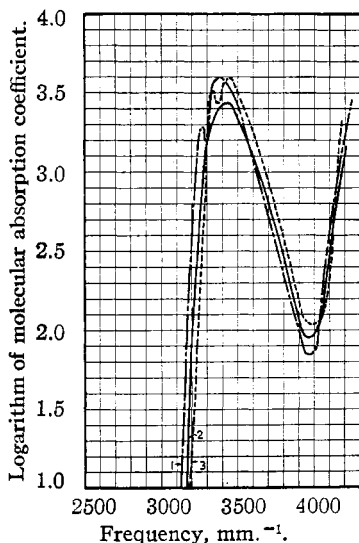


Fig. 2.—1, Hydroquinone; 2, hydroquinone monomethyl ether; 3, hydroquinone dimethyl ether.

values corresponding to such a mixture of methyl ethers and extending the calculations out to the regions where both compounds influence the absorption curve of the mixture, the values indicated by the circles in Fig. 1 are obtained. It will be seen that the agreement is very good except near the top of the absorption band in the ultraviolet. The disagreement within this region probably indicates that our assumption of the close similarity of the curves of the methyl ethers to the corresponding hydroxy compounds does not hold within these limits. Studies of solutions of this tautomeric mixture in other solvents are being carried on.

The curves for the quantitative absorption spectra for quinone, quinonechlorimine and quinonedichlorodiimine are shown in Fig. 3, and the curves for quinone and quinonedioxime are shown in Fig. 4.

In the latter figure a curve has been included for the absorption spectrum that we should expect to obtain from a sample of pure quinoneoxime. That portion of the curve has been omitted where the previously made assumptions do not seem to apply. The frequencies of maximum absorption for the bands in the visible which are indicated in Fig. 4 and in the table are the same as those found for quinoneoxime in the tautomeric mixture. The compounds in Fig. 3 are the derivatives of quinone in which the ketonic oxygen has been replaced by the $=\text{NCl}$ group, and the compounds in Fig. 4 are the derivatives of quinone in which the ketonic oxygen has been replaced by the $=\text{NOH}$ group.

The progressive changes which are noted on the successive substitution of the $=\text{NCl}$ group for a $=\text{O}$ group in quinone are the shifting of the ultraviolet band toward the visible and a shifting of the bands in the visible

region toward the ultraviolet. In quinonedichlorodiimine we find only one intense band. The ultra-violet band as we pass through the series successively persists over a greater dilution being least for quinone and greatest for quinonedichlorodiimine. In Fig. 4, similar changes are noted for the $=\text{NOH}$ compounds. The curves for quinonechlorimine and the calculated one for quinoneoxime are very similar to each other, as are also the curves for quinonedioxime and quinonedichlorodiimine.

The quantitative absorption curves for the reduction products of each: quinone, quinoneimine and quinonediimine, namely, the curves for hydroquinone, *p*-aminophenol and *p*-phenylenediamine, are given in Fig. 5.² The solvent used was absolute ether. *p*-Aminophenol and *p*-phenylenediamine may be considered as derived from hydroquinone by

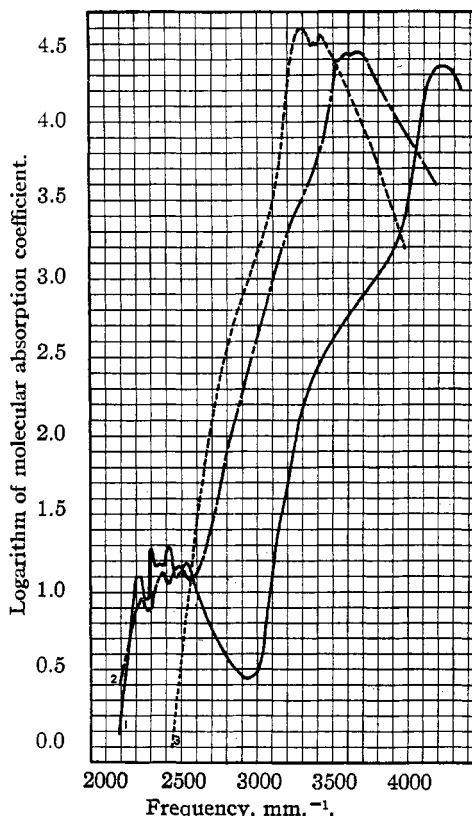


Fig. 3.—1, Quinone; 2, quinone chlorimine; 3, quinonedichlorodiimine.

FREQUENCY NUMBERS OF BANDS IN ETHER SOLUTIONS

Quinoneoxime.....	2095	2210	2349	2456	3417			
Quinoneoxime methyl ether....	2187	2301	2447	2575	3234			
<i>p</i> -Nitrosoanisole.....				2989	3493			
Hydroquinone.....				3270	3373			
Hydroquinone methyl ether....					3415			
Hydroquinone dimethyl ether...				3345	3436			
Quinone.....	2125	2200	2236	2317	2360	2429	3580	4123
Quinonedioxime.....					3212			
Quinonechlorimine.....	2155	2267	2380	3459	3557			
Quinonedichlorimine.....				3184	3260	3305		
<i>p</i> -Aminophenol.....				3228				
<i>p</i> -Phenylenediamine.....				3099				

² References to previous work upon the absorption spectra of quinone, its methyl ethers, hydroquinone, *p*-aminophenol and *p*-phenylenediamine may be found in Volume V of the "International Critical Tables."

the replacement of the hydroxyl groups of hydroquinone with amino groups. The regular changes in absorption curves which accompany these replacements are, first, a shifting of the absorption toward the visible region and, second, a decrease in its persistence.

The question of the structure of quinone and its derivatives has received considerable attention in the past. The assignment of the di-

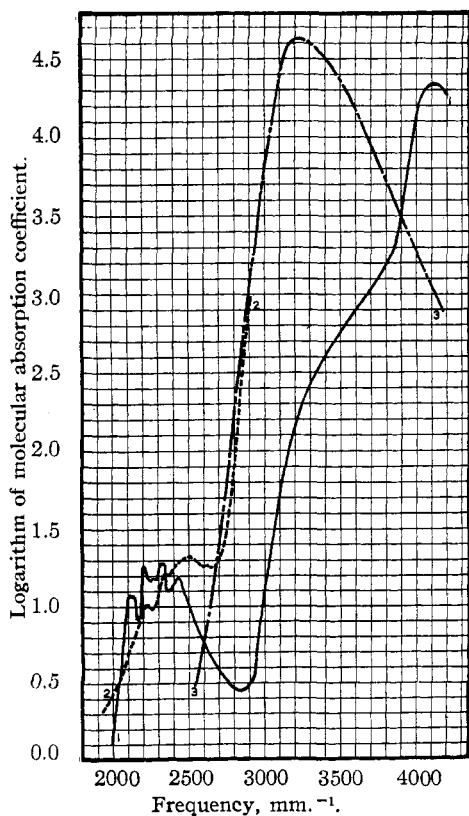


Fig. 4.—1, Quinone; 2, quinoneoxime (calcd.); 3, quinonedioxime.

ketonic formula to quinone has been favored by evidence obtained by Garner and Sugden³ from parachor measurements, by Pascal⁴ from magnetic susceptibility measurements and by Light⁵ from absorption spectra data. The most recent data which favor the peroxidic formula were presented by Binder⁶ from heats of combustion. If the quinone derivatives are better represented by the peroxidic structure, then the general location and the height of the absorption bands of these derivatives should resemble those of hydroquinone and its derivatives, since under such an assumption, they would all contain a benzenoid nucleus. That there is, however, no such resemblance is evident from a comparison of the curves in Figs. 2 and 5 with those in Figs. 3 and 4. The compounds of known benzenoid structure of Figs. 2 and 5 have no absorption in or adjacent to the visible region of the spectrum and the absorption band in the ultraviolet is only about one-tenth as persistent as the ultraviolet band for the quinone derivatives. Our conclusion, therefore, is that the diketonc structure best explains the data obtained from the absorption spectra.

³ Garner and Sugden, *J. Chem. Soc.*, 2877 (1927).

⁴ Pascal, *Bull. soc. chim.*, [4] 9, 339, 812 (1911).

⁵ Light, *Z. physik. Chem.*, 122, 414 (1926).

⁶ Binder, *Chem.-Ztg.*, 45, 1114 (1921).

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Experimental

The instruments and methods used for obtaining the quantitative absorption curves and points of maximum absorption have been described.⁷ In the purification of all the compounds except quinone, *p*-aminophenol and *p*-phenylenediamine the final recrystallization was carried out from a solvent which showed no selective absorption between 2300 and 7500 Å. The material which on solution in ether produced the tautomeric mixture of quinoneoxime and *p*-nitrosophenol was prepared by the action of nitrous acid on phenol. The product was first crystallized from water using charcoal for decolorizing, and finally from ether; m. p. 128–129°.

***p*-Nitrosoanisole.**—*p*-Nitrosoanisole was reduced to the corresponding hydroxylamine and this compound was oxidized to the nitroso derivative by the method described by Rising.⁸ The product was purified by distillation with steam and was crystallized from hexane; m. p. 22.5°.

Quinoneoxime methyl ether was obtained by the methylation of quinoneoxime with diazomethane.⁹ It was crystallized from hexane; m. p. 82°.

***p*-Quinone** was prepared by the oxidation of hydroquinone with chromic acid. The crude product was purified by several successive sublimations; m. p. 116°.

Quinonechlorimine was obtained by the action of sodium hypochlorite on the hydrochloride of *p*-aminophenol.¹⁰ The material was crystallized from hexane; m. p. 87°.

Quinonedichlorodiimine resulted from the oxidation of *p*-phenylenediamine hydrochloride with sodium hypochlorite.¹⁰ The product was crystallized from hexane; m. p. 128° with decomposition.

Quinonedioxime was prepared by the action of hydroxylamine hydrochloride on quinoneoxime.¹¹ The material was crystallized from ether; m. p. 242° with decomposition.

Hydroquinone.—Kahlbaum's product was crystallized from water using charcoal for decolorizing; m. p. 169°.

Kahlbaum hydroquinone monomethyl ether was crystallized from hexane; m. p. 55.5°.

The dimethyl ether of hydroquinone was obtained by crystallizing an Eastman product from 95% alcohol; m. p. 56°.

Eastman *p*-aminophenol was purified by sublimation at 180° under reduced pressure (2 mm.); m. p. 184° with decomposition.

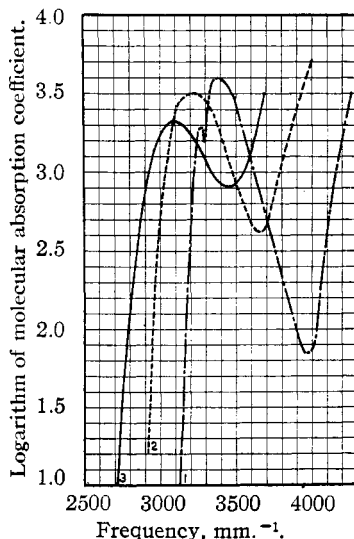


Fig. 5.—1, Hydroquinone; 2, *p*-aminophenol; 3, *p*-phenylenediamine.

⁷ Anderson and Gomberg, *THIS JOURNAL*, 50, 203 (1928); Anderson, *ibid.*, 51, 1889 (1929).

⁸ Rising, *Ber.*, 37, 44 (1904).

⁹ Von Pechmann and Seel, *ibid.*, 31, 299 (1898).

¹⁰ Willstätter and Mayer, *ibid.*, 37, 1498 (1904).

¹¹ Lobry de Bruyn, *Rec. trav. chim.*, 13, 109 (1894).

Eastman's *p*-phenylenediamine was sublimed at 200° under reduced pressure (2 mm.); the pure white product melted at 140°.

Summary

1. The quantitative absorption curves for ether solutions of *p*-nitrosoanisole, the methyl ether of quinoneoxime and of quinoneoxime have been determined. The spectroscopic results indicate that quinoneoxime and *p*-nitrosophenol are in tautomeric equilibrium in ether solutions in the ratio of approximately seven parts of the former to three parts of the latter.

2. The quantitative absorption spectra of ether solutions of quinone, quinoneoxime, quinonedioxime, quinonechlorimine and quinonedichlorodiimine together with the curve for the tautomeric mixture of quinoneoxime, and *p*-nitrosophenol have been obtained. The conclusion is drawn from these data that the diketonic or quinonoid formula represents the correct structure for quinone and the quinone derivatives.

3. The quantitative absorption curves for the ether solutions of hydroquinone, *p*-aminophenol, *p*-phenylenediamine, hydroquinone monomethyl ether and hydroquinone dimethyl ether have been obtained.

4. The frequencies of maximum absorption for all the compounds studied in this investigation have been ascertained and these values are presented in a table.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. IX. REACTIONS BETWEEN PERSULFIDES OF HYDROGEN AND ORGANIC COMPOUNDS

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The persulfides of hydrogen bear the same relationship to liquid hydrogen sulfide as does hydrogen peroxide to water. Since hydrogen sulfide dissolves organic bodies very readily, more readily than does water, one would expect that the hydrogen persulfides would react with organic compounds more readily than does hydrogen peroxide but in a similar manner.

Up until the work of Bloch and Höhn,² Schenck and Falcke³ and Brunner and Vuillenmuir⁴ the properties of the hydrogen persulfides were either little known or the data given were incorrect.

The reactions of hydrogen peroxide on organic compounds were in-

¹ This work is from a portion of a thesis presented to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Bloch and Höhn, *Ber.*, **41**, 1961-1980 (1908).

³ Schenck and Falcke, *ibid.*, **41**, 2600 (1908).

⁴ Brunner and Vuillenmuir, *Schweiz. Med. Wochschr.*, **46**, 436 (1908).