# THE ABSORPTION SPECTRA OF A SERIES OF ORGANIC MOLECULAR COMPOUNDS<sup>1</sup>

## W. H. HUNTER AND E. H. NORTHEY<sup>2</sup>

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

## Received February 24, 1933

Pfeiffer (1) and others have investigated the colored molecular compounds resulting from quinones with aromatic hydrocarbons, ethers, or amines. Pfeiffer has classified these compounds with the quinhydrones and has shown that a series extends from the intensely colored quinhydrones existing as crystalline compounds, through colored complexes difficult to crystallize, to complexes impossible to crystallize and identified largely by a slight color change on mixing the liquid components. These latter "molecular compounds" are tied by forces which are weak in comparison with the intermolecular forces in the crystallize out separately. Foreign solvents tend to dissociate the compounds and as a result Beer's law does not hold.

We undertook a spectroscopic study of the more weakly tied compounds of this type in the hope of extending the series of molecular compounds to loosely tied complexes which had escaped detection because the color change occurred in the ultra-violet or was too slight to be seen with the eye. There was also the possibility that the "solvent effect" of absorption spectroscopy could be linked with these color changes. Foremost, however, there was the hope that a correlation between color and oxidation-reduction potentials might be established.

#### RESULTS

We have carried out quantitative light absorption measurements on the five quinones—chloroquinone, benzoquinone, toluquinone, xyloquinone, and duroquinone—in a melted state and in the absence of any solvent. The resulting curves are compared with the light absorption of equimolecular mixtures of these quinones with various aromatic ethers, hydrocarbons, and

<sup>&</sup>lt;sup>1</sup> This article is based upon the thesis of E. H. Northey submitted to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1930. The manuscript was prepared by the junior author after the death of Dr. Hunter in 1931.—L. I. Smith.

<sup>&</sup>lt;sup>2</sup> du Pont Fellow in Chemistry, 1929-1930.

amines. Thirty-three such combinations were investigated. No third component was used as solvent because of the probable dissociation it would involve; instead a thin layer of the liquid mixture was employed, necessitating the use of special absorption cells and technique. However, it is convenient to refer to the nonquinoid component of the equimolecular mixture as "solvent." This will be done in the subsequent discussion.

Practical considerations limited our choice of components. Melting points and vapor pressures of the pair had to be nearly equal, otherwise changes in composition occurred during measurement. Thus di-, tri- and tetra-chloroquinones were eliminated on account of their high melting points,



FIG. 1. CHLOROQUINONE

and benzene, toluene, and hexamethylbenzene were eliminated on account of their high vapor pressures.

The results as shown in figures 1 to 7 are expressed in terms of the extinction coefficient as defined by the Bunsen-Roscoe law:

$$K = \frac{1}{d} \log_{10} \frac{I_0}{I}$$

where d is the thickness of absorbing layer in centimeters. These curves compare the absorption of a quinone with the absorption of its molecular compounds with various "solvents," assuming complete combination. Actually an equilibrium mixture was undoubtedly present and account



should be taken of the absorption of uncombined quinone,<sup>3</sup> but since the dissociation constants were lacking, no correction could be made. However,

<sup>3</sup> The solvents are nearly transparent in the region studied and their slight absorption was corrected for during measurement.



it was of considerable interest to replot the data on the assumption of no compound formation, i.e., it was assumed that the only effect of the "solvent" was simple dilution, and by calculating back to the absorption of quinone with solvent removed, curves were obtained which show the "sol-



vent effect" to better advantage. Calculated in this way, and granting the assumptions, the absorption curves of a pure quinone and its various "solutions" should be identical.

Let K = the measured extinction coefficient of a quinone in solution, and K' = the extinction coefficient with solvent removed. K' will differ from K only in the thickness of the absorbing layer if the solvent is transparent and otherwise inert. The relationship is:

$$K' = \left[1 + r\frac{M_s S_q}{M_q S_s}\right] K$$

 $\mathbf{or}$ 

$$\log K' = \log K + C$$

where

$$C = \log\left[1 + r \frac{M_s S_q}{M_q S_s}\right]$$

ГΑ	в	$\mathbf{LE}$	1
----	---	---------------	---

Values of $C f$	or equin	olecular	mixtures	of	quinone	and	"solvent"
-----------------	----------	----------	----------	----	---------	-----	-----------

	CHLORO- QUINONE	QUINONE	TOLU- QUINONE	DURO- QUINONE
Dimethylaniline	0.35	0.41	0.33	0.25
Hydroquinone dimethyl ether	0.36	0.42	0.34	0.26
Resorcinol dimethyl ether	0.36	0.42	0.34	0.26
Veratrole	0.35	0.41	0.33	0.25
Anisole	0.31	0.36	0.29	0.22
<i>p</i> -Xylene	0.34		0.32	
Mesitylene	0.37	(	0.35	
Durene	0.40		0.38	
Dibenzyl	0.38		0.36	
	·			

and  $M_s$  = molecular weight of "solvent,"

 $M_q$  = molecular weight of quinone,

 $S_s = \text{density of "solvent,"}$ 

 $S_q$  = density of "quinone," and

r = mole ratio of "solvent" to "quinone."

Hence if  $\log K$  is replotted as  $\log K'$  the curve will simply be raised by an amount equal to C.

Densities of "solvent" and quinone must be known slightly above the melting point to make use of the formula. Most of the data needed were found in the literature, but rough determinations had to be made on the quinones. These densities are: for chloroquinone,  $d^{60^\circ}$  1.38; toluquinone,  $d^{70^\circ}$  1.07; duroquinone,  $d^{116^\circ}$  1.02. A value for quinone was found in the literature, while insufficient xyloquinone was available for a determination.

The calculated values of C are given in table 1.

880

### DISCUSSION OF RESULTS

Figure 8 shows the data on duroquinone replotted in terms of  $\log K'$ . It is apparent that there is an effect of "solvent" other than simple dilution, since the "solution" curves deviate from that of the pure quinone. In the case of anisole this deviation is relatively small and is comparable with changes in the absorption spectrum of any substance observed by changing from one solvent to another. The increased effect of veratrole is still of the order of solvent effects and would be so ascribed in the absence of other



FIG. 8. DUROQUINONE

data. There can be little doubt, however, that if the solvent effect is met with in the case of duroquinone it is the result of the same influences causing color changes in the case of chloroquinone. Since Pfeiffer has demonstrated that these color changes are a part of molecular compound formation, it appears that we have bridged the gap between true molecular compounds and one type of solvent effect.

Comparison of figures 1 to 7 for any one "solvent" shows that the difference between the "solution" curve and quinone curve increases in the order duroquinone, xyloquinone, toluquinone, quinone, chloroquinone. In order to put these differences on a numerical basis we have arbitrarily measured the areas between the quinone curve,  $\log K = 1.5$ , and the "solution" curves. The unit of area has no significance and the choice of log K at 1.5 was for convenience, as such choice does not affect the order of the results.

In figure 9 we have plotted these areas against Conant and Fieser's (2) values of  $\pi_s$ , the reduction potential in volts, of the respective quinones. Two generalizations can be drawn from these data:

I. In a series of quinones the change in the absorption spectrum, brought about by a solvent capable of forming molecular compounds, increases with increasing oxidation-reduction potential of the quinones.



II. The order in which "solvents" fall with respect to increasing effect on the absorption spectrum of a quinone is independent of the quinone studied.

The significance of these findings with respect to color theories is evident; however, additional experimental work along several lines is necessary in order to place the results here obtained in their proper relation. Since no further work is possible in the near future, the results are published in the hope that they may be of use elsewhere.

# EXPERIMENTAL

# Apparatus

All measurements of light absorption were carried out quantitatively by means of a Judd Lewis sector photometer (Hilger H-41) and Hilger E-2 spectrograph. The light source was an under-water tungsten spark (3). Spectra were photographed on Wratten and Wainwright panchromatic plates. Points of equal density on paired spectra were found by use of a Moll type A microphotometer especially adapted to the work by adding a longer galvanometer scale, a more powerful light source, and an elevating lever for rapid shift from one spectrum to the other. Match points were marked on the emulsion by a fine scratch and their wave lengths were later read off from calibrated wave length scales photographed on the plate.

Instead of diluting with a solvent to obtain high values of the extinction coefficient we had to use extremely thin layers of the melted compounds. Absorption cells as shown in figure 10 were therefore constructed. Fused quartz plates  $2 \times 2$  cm. square  $\times 3.5$  mm. thick, ground optically flat to a tolerance of 0.001 mm. were spaced apart by thin strips of pure gold, 2 mm. wide by 2 cm. long, which were laid along two sides and the bottom. The



Fig. 10

thickness of the gold varied from 0.075 to 0.005 mm. depending on the range of log K required, the thinnest layer permitting a value for log K of 3.5 to be measured. All metal parts of the cell were heavily gold plated to resist corrosion by the quinones.

As it was necessary to keep the mixture molten while spectra were being taken, a cell heater was constructed to set on the table of the photometer in place of the usual cell supports. This was of sheet iron construction inside and out, insulated electrically with mica and thermally with magnesia. Windows of 2-cm. brass tubing provided passage for the two light beams of the photometer. The two windows at the end nearest the spectrograph were closed on the inside with thin quartz discs to prevent vapors from condensing on the collimating lenses of the photometer. The other windows were left open to prevent the accumulation inside the heater of sufficient vapor to affect the results. Heat was applied electrically by resistance wire wound around the core and regulated with a lamp bank to give a temperature about two degrees above the melting point of the substances studied.

## Technique

In the assembly of the absorption cells, the quartz plates were first cleaned with extreme care. All subsequent handling was done with smooth-jawed brass forceps. After assembly, the cell thickness was made uniform by adjusting the seven small screws bearing against the U-shaped strip of brass. The cell was viewed by reflected light from a Pyrex mercury arc, and adjustment was varied until the interference bands which appeared were lined vertically with the cell and as few in number as possible. A minute variation in thickness across the cell was of slight concern, since in measuring both cell thickness and light absorption an average value was obtained; variation from top to bottom caused a gradation in density across the spectrum, however, and was avoided.<sup>4</sup> The empty cell after adjusting as above, was held at the slit of a spectrograph and illuminated by a powerful continuous light source.<sup>5</sup> The spectrum of the empty cell was photographed and adjacent to it the mercury arc spectrum. The number of dark interference bands between two lines in the mercury arc was counted. The cell thickness was then found using the formula:

$$d = \frac{\frac{n}{2}}{\frac{1}{\lambda_1} - \frac{1}{\lambda_2}}$$

where d = thickness of cell, and

n = the number of dark bands between wave lengths  $\lambda_1$  and  $\lambda_2$ . Unless the cell was of uniform thickness from top to bottom, the interference bands were sloped and indistinct.

Two cells were placed in the heater. One contained the melted compound; the other, containing the "solvent," served to correct for light reflected from the faces of the first cell and for light absorbed by the "solvent." In taking the spectra of pure quinones this second cell was empty, the two quartz plates being spaced to avoid interference bands.

Equimolecular amounts of the quinone and "solvent" were weighed into a test tube made of an 18-cm. length of 8-mm. Pyrex tubing. A 20cm. length of 3-mm. tubing drawn to a tip at one end made a sort of elongated medicine dropper for transferring the melted substance from test tube to absorption cell. The tip of the dropper was placed at the space between the quartz plates. Providing the cell had been properly cleaned,

<sup>&</sup>lt;sup>4</sup> We are indebted to Professor Valasek of the Physics Department for suggesting the method of measuring cell thickness.

<sup>&</sup>lt;sup>5</sup> Hilger E. I. spectrograph and 500-watt projection bulb.

surface tension then filled the cell completely. The cell was always inspected to see that no air bubbles remained.

# Preparation and purification of materials

Dimethylaniline. The commercial product was treated with acetic anhydride, carefully fractionated under vacuum, and finally purified by three crystallizations from its own mother liquor.  $n_{\rm p}^{20}$  1.5570; given in the literature, 1.55873.

Hydroquinone dimethyl ether. Kahlbaum's product was twice fractionated in vacuo. Melting point 56°C.; given in the literature, 56°C.

Resorcinol dimethyl ether. Resorcinol was methylated with dimethyl sulfate and the crude product purified by steam distillation, vacuum distillation, treatment with metallic sodium, and again vacuum distillation. Boiling point, 82.5–84°C. at 5 mm.; given in the literature, 216.5–217.7°C. at 760 mm.

Veratrole. Guaiacol was methylated with dimethyl sulfate and the product twice vacuum distilled. The fraction boiling at 100–106°C. at 18 mm. was partially frozen and the crystals separated. This was repeated six times, the melting point rising to  $22^{\circ}$ C.; given in the literature, 23°C.

Anisole. Anisole was purified by vacuum distillation. Boiling point, 65°C. at 20 mm.  $n_{\rm p}^{21.8}$  1.5153; given in the literature, 1.51503.

*p-Xylene.* Kahlbaum's product was used without purification. Melting point,  $12-14^{\circ}C$ ; given in the literature,  $16^{\circ}C$ .

Mesitylene. Eastman's product was used without purification.  $n_{\rm p}^{14.6}$  1.5000; given in the literature, 1.4966.

Dibenzyl. This was made according to the directions of Cannizzaro and Rossi (4). The crude product was recrystallized three times from alcohol using charcoal. It was then recrystallized twice from purified ether. Melting point,  $51.5-52.5^{\circ}$ C.; given in the literature,  $52.5^{\circ}$ C.

Tolane. Stilbene dibromide was treated under a reflux condenser for eight hours with a slight excess of saturated alcoholic potassium hydroxide. The potassium bromide was filtered off and the liquid returned to the flask with addition of a small amount of solid potassium hydroxide for another eight hours. The product was poured into ice water; the oily layer was separated, dried, and distilled *in vacuo*. The tolane fraction was recrystallized from alcohol four times, twice vacuum distilled, and again crystallized from absolute alcohol. Melting point,  $60^{\circ}$ C.; given in the literature,  $60^{\circ}$ C.

*Chloroquinone.* A mixture of 30 g. of chlorohydroquinone, 300 cc. of purified ether, and 200 g. of finely divided lead dioxide was stirred for 10 minutes, after which the lead dioxide was filtered off and washed well with ether. The combined ethereal solutions were evaporated to a volume of

200 cc. and crude chloroquinone crystallized out by freezing in a carbon dioxide-ether bath. Repeated recrystallizations from absolute ether gave a product melting at  $57^{\circ}$ C. (literature,  $57^{\circ}$ C.).

Quinone. Crude quinone was purified by several sublimations. Melting point, 113.5–114.5°C.; given in the literature, 115.7°C.

*Toluquinone.* This was prepared from *o*-toluidine by Nietzki's method (5). It was purified by repeated recrystallization and sublimation. Melting point,  $67-67.5^{\circ}$ C.; given in the literature,  $69^{\circ}$ C.

*p-Xyloquinone. p*-Xylidine was oxidized by Nietzki's method (5). It was purified by repeated recrystallization and sublimation. Melting point,  $123-124^{\circ}$ C.; given in the literature,  $125^{\circ}$ C.

Durene and duroquinone. These substances were obtained in a pure state from Professor L. I. Smith, to whom we are very deeply grateful. The melting points and boiling points given are uncorrected. Refractive indexes were determined with an Abbé refractometer. All quinones were repurified just preceding use.

#### SUMMARY

1. The absorption spectra of chloroquinone, benzoquinone, toluquinone, xyloquinone, and duroquinone were measured quantitatively in the absence of solvent.

2. A technique is described for obtaining quantitative light absorption measurements on thin layers of liquids or melted solids.

3. The absorptions of equimolecular mixtures of the above quinones with aromatic hydrocarbons, ethers, and amines were measured. A variation in the effect of these "solvents" on the spectra of the quinones was observed, ranging from very pronounced color changes attributed to molecular compound formation to slight changes of the order of "solvent effects."

4. The changes from the absorption spectra of quinones in a pure state to the spectra in molecular compound forming "solvents" have been correlated with the known oxidation-reduction potentials of the quinones.

5. Two generalizations have been found:

I. In a series of quinones the change in the absorption spectrum brought about by a "solvent" capable of forming molecular compounds, increases with increasing oxidation-reduction potential of the quinones.

II. The order in which "solvents" fall with respect to increasing effect on the absorption spectrum of a quinone is independent of the quinone studied.

We wish to express our thanks to both the Physics Department and the Biophysics Department of the University of Minnesota for their valuable aid in supplying equipment and suggestions as to its use.

### REFERENCES

- (1) PFEIFFER, P.: Organische Molekülverbindungen. Enke, Stuttgart (1927).
- (2) CONANT AND FIESER: J. Am. Chem. Soc. 45, 2208 (1923).
- (3) Bur. Standards Scientific Paper No. 440, p. 129.
- (4) CANNIZZARO AND ROSSI: Ann. 121, 250 (1862).
- (5) NIETZKI: Ann. 215, 159 (1882).