THE ABSORPTION SPECTRA OF PHENOQUINONE, 2,5-DIANILINOQUINONE, 2,5-DIANILINOQUINONEANIL, AND 2,5-DIANILINOQUINONEDIANIL (AZOPHENINE)

By D. S. PRATT and H. D. GIBBS[1]

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Two text figures

In the study of the compounds which cause the red color of phenol[2] it was pointed out that the coloration is due to the oxidation of phenol to quinone with the subsequent condensation to phenoquinone, although physico-chemical methods would be necessary to prove the presence of the latter compound. The most satisfactory method appeared to be based upon the absorption spectra of the compounds in question.

Phenoquinone, crystallized from ligroine, was dissolved in absolute alcohol, and the absorption spectrum photographed in the manner described in our previous work.[3] The absorption curves, plotted with logarithms of the dilutions and oscillation frequencies, are shown in fig. 1, and the curves of quinone and phenol in alcohol are included for purposes of comparison.

In alcohol, the color band shows in one-tenth molar solution and closely resembles that of quinone. Dilutions of this solution to hundredth and thousandth molar concentrations give curves that are not continuations of the tenth molar and of each other. This discontinuity upon dilution is not shown by quinone and phenol, and since these compounds follow Beer's law it is evident that dilutions of phenoquinone solutions do not give the expected concentrations of phenoquinone. This is due to dissociation which may be expressed by the equilibrium equation:

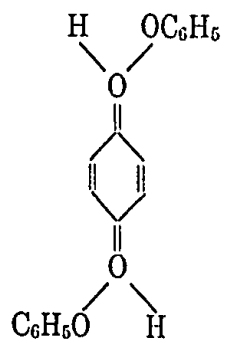
$$C_6H_4O_2 + 2C_6H_5OH \rightleftharpoons C_6H_4O_2 \cdot 2C_6H_5OH.$$

In order to test the validity of this assumption, we have dissolved in alcohol quantities of quinone and phenol calculated for tenth molar solution of phenoquinone and find that the absorption curve of this solution coincides with that obtained by dis-

[1] Associate professor of chemistry, University of the Philippines.
[2] Gibbs, *This Journal, Sec. A* (1908), 3, 364.
[3] *This Journal, Sec. A* (1912), 7, 371; (1913), 8, 33.

solving phenoquinone crystals in alcohol. These two solutions are in fact identical. Since the curve obtained with tenth molar solutions so closely resembles the quinone curve, and for other reasons, it is evident that the actual amount of phenoquinone in solution at this concentration is very small.

If the above equilibrium reaction is correctly represented, an increase in the concentration of phenol should result in a greater concentration of phenoquinone, and in phenol as a solvent the dissociation of phenoquinone should be at a minimum. The curves obtained with an excess of 8 equivalents of phenol and in pure phenol show this assumption to be justified. The most striking characteristic of these curves is the change from a definite absorption band shown in quinone to a mere step off in phenoquinone in phenol and also the greatly reduced concentration at which the incipient band appears. From this it is evident that the red color of phenoquinone is largely due to general absorption, and it is probable that the isorropesis present in phenoquinone is quite different from that in quinone. This difference, it seems to us, is due to a loss of the free affinities of the two carbonyl groups, and may be best expressed by the oxonium structure



This representation accounts for the instability of the compound, the dissociation in solution, and the formation of its very unstable salts better than the formulas of Jackson and Oenslager [4] and of Willstätter and Piccard.[5]

The conditions existing in dianilinoquinone, dianilinoquinoneanil, and azophenine are quite different. In all of these compounds the quinone absorption band is well marked, and in

[4] *Ber. d. deutschen chem. Ges.* (1895), 28, 1614; and *Am. Chem. Journ.* (1896), 18, 1.

[5] *Ber. d. deutschen chem. Ges.* (1908), 41, 1458.

azophenine the isorropesis occurring between the two unsaturated nitrogen atoms in the para position produces the same effect as the carbonyl groups. Since the absorption bands are well developed and in much the same positions when phenol is employed as the solvent, it is evident that the absence of a well-marked phenoquinone band in this portion of the spectrum is not to be attributed to this solvent.

The dilution at which the band characteristic of the quinoid structure makes its appearance is dependent upon the nature of the adjacent groups, since this band is shown in tenth molar solutions of quinone and in thousandth or ten-thousandth molar solutions of the other compounds mentioned. The argument employed by Baly, Tuck, and Marsden [6] that the bands of the

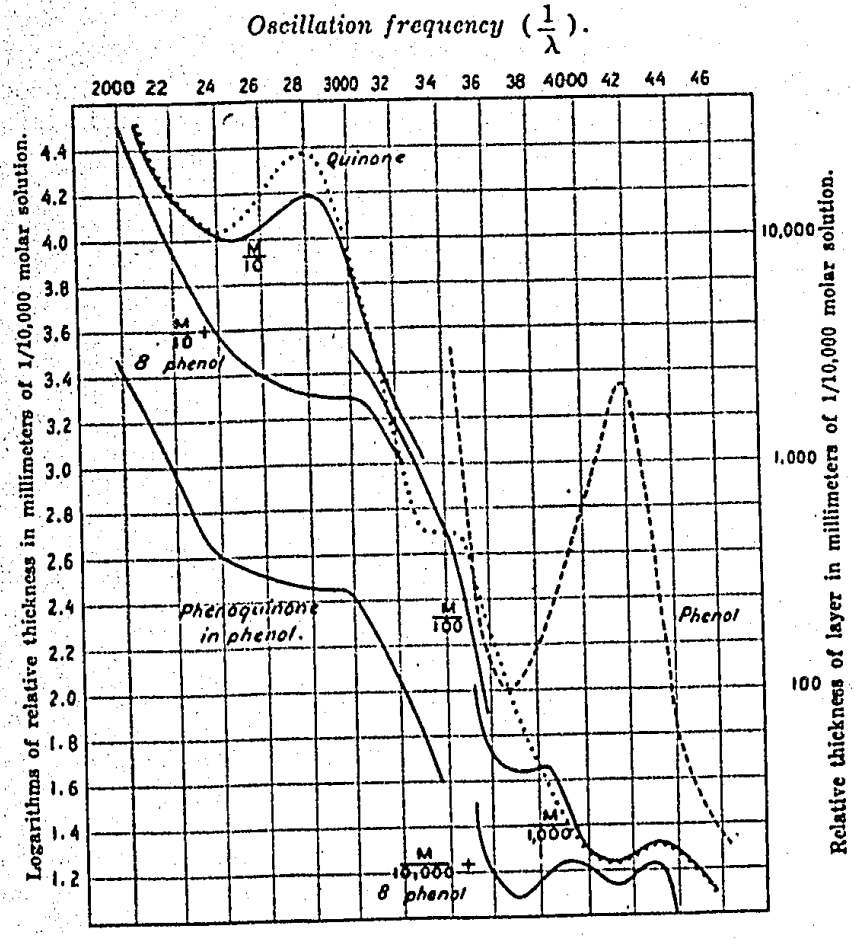


FIG. 1.—Full curves = phenoquinone.
The upper in alcohol, the middle in alcohol with 8 equivalents of phenol, and the lower in pure phenol.
Dot curve = quinone in alcohol.
Dash curve = phenol in alcohol.

[6] *Journ. Chem. Soc. London* (1910), 97, 588.

nitrophenols in presence of alkali are not quinone bands for the reason that they appear at greater dilutions than in quinone itself is thus seen to be without weight.

In order to prove that phenoquinone is produced in phenol by oxidation, we have exposed colorless phenol in open vessels to the action of sunlight until it developed a decided red color, after three or four days, and then photographed its absorption spectrum. The curve was found to coincide with that of phenoquinone dissolved in phenol. The proportion of phenoquinone formed by the action of sunlight and oxygen in a given time can be estimated by comparison with the curves shown in fig. 1.

Fig. 1. The curves of quinone, phenol, phenoquinone in alcohol, phenoquinone plus 8 equivalents of phenol in alcohol, and phenoquinone in pure phenol are shown. Our curve of quinone practically agrees with that given by Baly and Stewart,[7] except that the small band in the benzene region heading at $1/\lambda=4100$ is not shown in their charts. Hartley, Dobbie, and Lauder[8] show this band highly developed, but it is probable that the pure compound will show no band in this region of the spectrum. Since quinone is so readily reduced by alcohol in ultra-violet light, it is reasonable to attribute this incipient band to the presence of small quantities of quinol.

The curves of phenoquinone in alcohol in tenth, hundredth, and thousandth molar concentrations have been previously described. The absorption band at $1/\lambda=3700$ is due to phenol and that at $1/\lambda=4100$ to quinone. The curve of phenoquinone with 8 equivalents of phenol obtained with hundredth molar solution is not shown on the chart, since it is almost a straight line and lies very close to that of hundredth molar phenoquinone. The phenol band at $1/\lambda=3700$ shows in this solution at log. 1.1, since the phenol is present at one-thousandth molar concentration.

Fig. 2. Since dianilinoquinone is insoluble in alcohol and in the usual diactinic solvents, it is necessary to employ glacial acetic acid to cover approximately the full range of the absorption spectrum. In order to obtain comparisons of the color band of this compound with those of dianilinoquinoneanil and azophenine, we have also used solutions in aniline and in phenol. The curves are shown in fig. 2.

[7] *Ibid.* (1906), 89, 507.
[8] *Rep. Brit. Assoc.* (1902), 99.

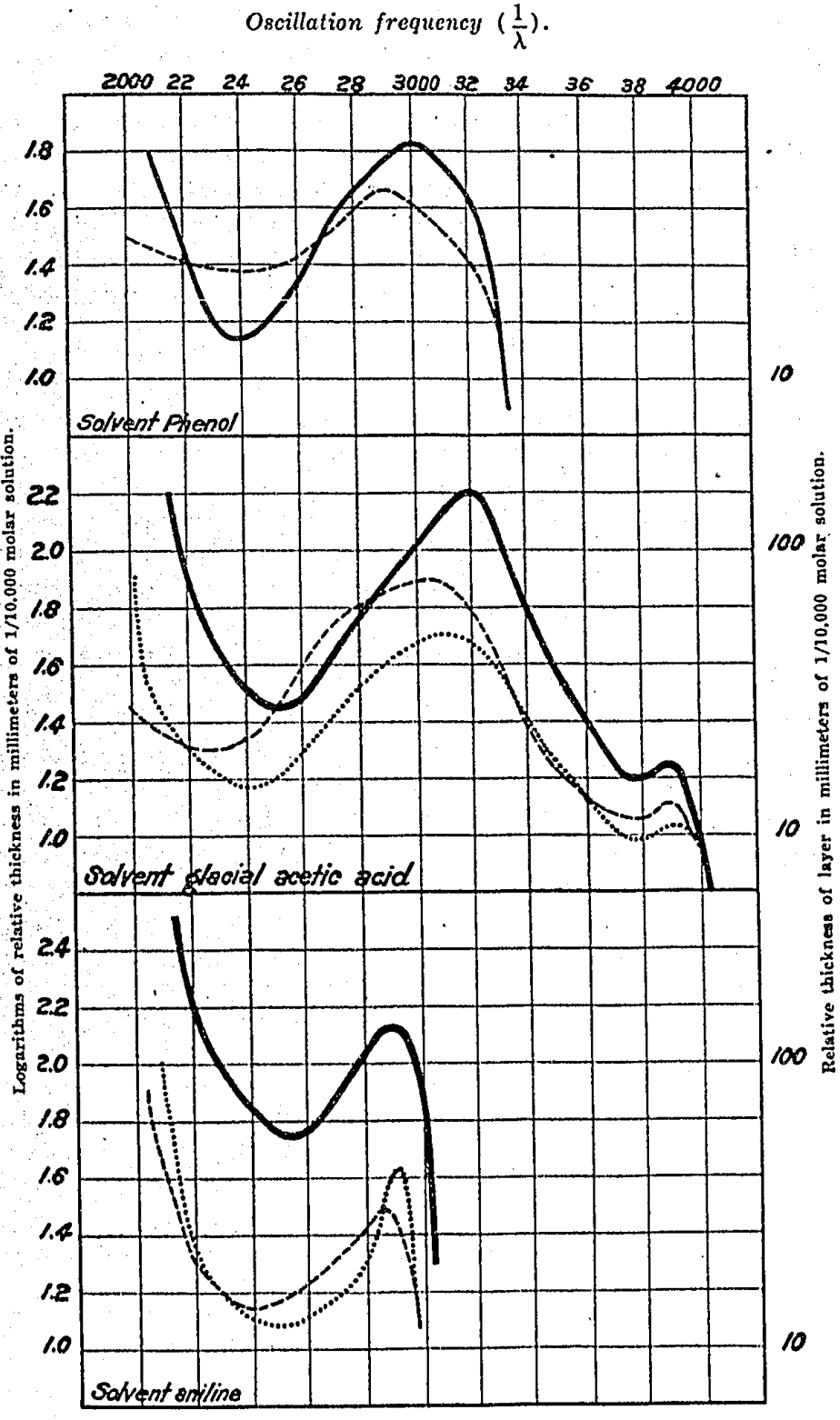


FIG. 2.—Full curve=2,5-dianilinoquinone.
Dot curve=2,5-dianilinoquinoneanil.
Dash curve=azophenine.

It is to be noted that the curves for dianilinoquinone are similar within the limits of the solvent in each case. The greatest variation due to the solvent is found in azophenine. The color band in phenol and in glacial acetic acid is much extended toward the red, and the general absorption is greatly increased over the curve shown in aniline. This condition is probably due to the acid nature of the solvents, phenol and acetic acid. The color bands of these three compounds are well defined in each solvent, and clearly indicate quinoid structure, which accords with the formulas assigned to them.

ILLUSTRATIONS

TEXT FIGURES

FIG. 1. Full curves=phenoquinone. The upper in alcohol, the middle in alcohol with 8 equivalents of phenol, and the lower in pure phenol.
Dot curve=quinone in alcohol.
Dash curve=phenol in alcohol.
2. Full curve=2,5-dianilinoquinone.
Dot curve=2,5-dianilinoquinoneanil.
Dash curve=azophenine.