holds and should give a value for ρ different from that obtained by means of equation (9). However, if the capillary is so adjusted that the plane of the cut surface is horizontal, the value for ρ obtained by both equations should be identical. This phenomenon has been actually observed and is represented diagrammatically in Fig. 2.

The capillary used here had been cut off improperly so that the cut surface formed an angle of 70° instead of 90° with the longitudinal axis of the capillary. The capillary radius was found equal to 13.4 μ by direct measurement of the smallest diameter of the oval orifice. In all subsequent calculations, this orifice was considered round and with a radius equal to the one measured. The critical pressure in water and the drop weight in a 0.1 N potassium chloride solution were then determined, first, when the capillary was vertical and the plane of the cut surface slanted, and, second, when the capillary was slanted to bring the orifice on a horizontal plane. The results and the calculated values were

Position of capillary	P_c, cm.	ρ, μ	W, mg.	ρ, μ
Straight	42.0	13.6	2.37	9.7
Slanted	39.5	14.5	3.32	13.7

From this, one must conclude that the ρ values obtained by the drop weight and critical pressure methods should certainly agree within 1μ to insure proper functioning of the capillary. It should be mentioned here that even this type of capillary can be used for some special polarographic work and will give good results as long as its position is rigidly fixed. Because of its extreme sensitivity to slight changes in position, it cannot be recommended for general use.

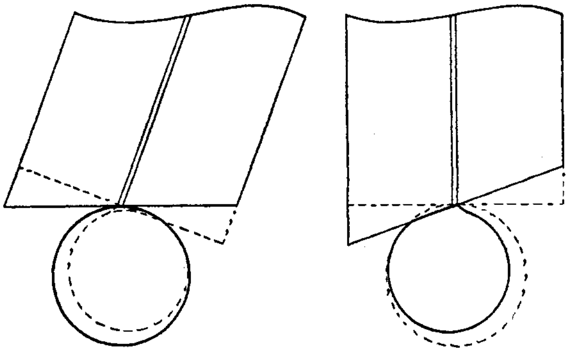

Fig. 2.—Graphical demonstration of the effect of position and improper cutting of the capillary on the drop size. Note that normal drops are obtained whenever the cut surface is perfectly horizontal.

Acknowledgment.—The author wishes to thank Mr. Howard Phipps and Dr. John Staige Davis, Jr., for financial support of this investigation.

Summary

Two factors have been proposed to serve as simple means for the complete characterization of all kinds of capillaries used for dropping mercury electrodes. These are the radius of the capillary orifice, ρ, and the capillary constant, κ, which is the pressure of mercury (in cm.) necessary to force 1 mg. of mercury through the capillary per second.

Various methods for their determination have been described which serve as checks for the proper behavior of the capillary.

Some abnormalities in the behavior of capillaries have been discussed.

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Molecular Compounds of the Quinhydrone Type in Solution

BY LEONOR MICHAELIS AND S. GRANICK

The intensely colored molecular compounds of the quinhydrone type are best known in the crystalline state.[1] In solution all of them dissociate to a very high degree, although not completely. Such compounds usually consist of two components of which one is on a higher oxidation level than the other. One component may be a quinone, or an aromatic nitro compound; the other a phenol, an amine, or even a hydrocarbon such as hexamethylbenzene. Most of the studies here reported were carried out with compounds of a quinone with some phenolic compound. Crystalline compounds of this kind have the following characteristics:

1. When quinone combines with hydroquinone, the stoichiometrical composition of the compound is Q_1B_1, where Q stands for the quinoid and B for the benzenoid component.
2. When quinone combines with a phenolic compound having only one unsubstituted OH group, the molecular compound is Q_1B_2. Examples are the quinone compound of phenol and of *p*-methoxyphenol.
3. Some quinhydrone-like compounds of "anomalous composition" have been described.[2] Their compositions were inferred, not from a straight-forward analysis of the solid, but by indirect methods involving dubious interpretations. Among all such compounds which can be prepared in the crystalline state, and which are of

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[1] P. Pfeiffer, "Organische Molekülverbindungen," Stuttgart, 1927. Some references to more recent papers are: I. Palacios and O. R. Foz, *Anales soc. españ. fís. quím.*, **34**, 799 (1936); G. Weiss, *J. Chem. Soc.*, **245** (1942) and **462** (1943); H. M. Powell, G. Huse and P. M. Cooke, *ibid.*, **153** (1943) and **435** (1943).

[2] R. Kremann, S. Sutter, F. Sitte, H. Strezelba and A. Dobotzky, *Monatsh.*, **43**, 269 (1922).

adequate stability, we encountered only one having the composition Q_2B_1, namely, quinone + phloroglucinol.

4. Quinone does not form a crystalline compound with any derivative of a phenolic compound in which the H atoms of all OH groups are substituted, such as the alkyl ether of phenol, or the di-alkyl ether of hydroquinone. Obviously the unsubstituted OH group is necessary for the formation of this type of molecular compound.

These characteristics, however, apply only for the solid compounds. In this paper it will be shown that in the dissolved state, all molecular compounds of the quinhydrone type are always of the composition Q_1B_1, regardless of their composition in the solid state, and even in such cases where no molecular compound exists at all in the solid state. As far as a comparison of various compounds in the same solvent can be carried out, one arrives at the conclusion that in the dissolved state the affinity of quinone is nearly the same for hydroquinone, its monomethyl ether, its dimethyl ether and its diethyl ether. It follows that problems concerning the composition and steric configuration of such compounds in the dissolved state cannot be dealt with on an equal footing with those holding for the solid state. The latter has been the subject of many experimental and theoretical studies[3] without a full understanding of the problem having been reached either with respect to the nature of the chemical bond, or to an explanation of the intense color, or to the general principle underlying the crystalline structure. Neither do the writers claim to have solved the problem, yet they have arrived at some definite experimental facts concerning the dissolved state which should have a bearing on any future general theory pertaining to the nature of such compounds.

It will be shown that all of the compounds of the quinhydrone type are highly dissociated in solution, and that the equilibrium within the limits of error can be expressed always as follows

$$qb/m = k \qquad (1)$$

where q and b are the total molar concentrations of the quinonoid and benzenoid components and m is the concentration of the molecular compound, instead of according to the more exact equation

$$(q - m)(b - m)/m = k \qquad (2)$$

In all cases, under all experimental conditions that can reasonably be applied, m is small, usually negligibly small, as compared with q and b. No method is available for the determination of the absolute value of m; only relative values can be obtained. This fact precludes any accurate determination of the association constant, k, for any one of these compounds. In solutions no evidence has yet been found for the existence of any compound other than Q_1B_1, both with respect to stoichiometrical composition and molecular size. The fact that, in the dissolved state, the substitution of the H in the OH group by the much more spacious CH_3 or C_2H_5 group, has no noticeable influence upon the formation of a molecular compound with a quinone, shows that, at least in the dissolved state, a hydrogen bond is not essential, as demonstrated by the formation of compounds such as quinone + hydroquinone–diethyl ether. The lack of any conspicuous steric hindrance caused by the alkyl group is compatible only with the assumption that in the dissolved state the molecular compound is always formed by superimposing the two rings upon each other, and not by a coplanar arrangement of the two rings.

The study of these molecular compounds in solution, where they exist only in extremely low concentration in equilibrium with their free components, depends on the relative intensity of their color. The free components absorb usually in the ultraviolet, and even where there is an additional absorption band in the visible spectrum as for quinone (with peak at 420 to 435 mμ, and with varying degree of fine structure (Fig. 5), according to the solvent) the molar absorption coefficient of this band at its maximum is very low. It is, for quinone, 17 to 19.8 depending on the particular solvent (whereas, for example, for regular dyestuffs of equivalent resonance structure it is of the order 10^4 to 10^5 at the peak of absorption). The quinhydrones also have a very high absorption coefficient at the peak of absorption, in or near the visible spectrum. Since the concentration of the molecular compound cannot be determined, its molar absorption coefficient cannot be determined either. However, it is always so large that even at those low concentrations at which they exist in equilibrium with the components, the optical density of the solution in or near the visible usually is due almost completely to the molecular compound alone, except for a small, sometimes negligible correction for the absorption due to the free components. This correction, then, consists in subtracting from the total optical density of the solution, that of its free components. Since always only a very small fraction (say 5% *in maximo* and usually very much less) of the components is used for the formation of the compound and the whole correction is usually small, no appreciable error is involved in subtracting the optical density due to the total concentration of the two components instead of subtracting the concentration of the uncombined part of the components. This correction is carried out by measuring the absorption against the pure solvent as a blank and subtracting the absorption due to the free components by calculation. Often a solution of one of the components in a proper concentration was used as a blank, and the correction for the other component was made by calculation. The

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(3) In addition to references quoted,[2] special attention should be given to some brief remarks on the subject in a paper by L. Pauling.[4] The authors are indebted to Professor Pauling also for further discussion and advice with respect to the problems involved.

(4) L. Pauling, *Proc. Natl. Acad. Sci.*, **25**, 577 (1939).

absorption was measured with the Beckman[5] photoelectric spectrophotometer which allows rapid and very precise readings of the transmission reproducible to within a fraction of 1%, from 215 to 1275 mμ.

The optical density, δ, of any solution is

$$\delta = \frac{I}{d}\log\frac{I_0}{I}$$

where I_0 is the intensity of light transmitted across the blank; I, that across the solution; and d, the thickness of the absorption cell in cm. The molar absorption coefficient of any single molecular species is $\epsilon_{\text{mol}} = \delta/c$ where c is the concentration of the substance in moles per liter.

The claim that all such molecular compounds in the dissolved state have the composition Q_1B_1, is based on the fact that the optical density due to the molecular compound is in all cases proportional to the concentration both of the Q component and of the B component, so that within the limits of error

$$\delta/qb = C$$

where the constant, C, depends on the particular compound and on the particular solvent used. This constant will, in what follows, be designated as ϵ_{st}, the "absorption coefficient of the molecular compound under standard conditions," in the particular solvent. Its significance will be discussed later.

Experimental Part

All substances were freshly purified either by sublimation, distillation, steam distillation, or recrystallization, and only quite fresh solutions were used, which is especially important for quinone.

In the diagrams, the corrected optical density of the solution, δ, is plotted against wave length in mμ. A few absorption spectra, in terms of the molar absorption coefficient, ϵ_m, for the single components are added.

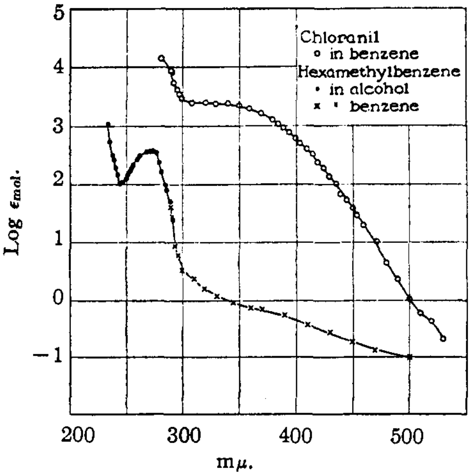

Fig. 1.

1. Examples of Compounds Having, in the Solid State, the Composition Q_1B_1

(a) Tetrachloroquinone + Hexamethylbenzene.—In Fig. 1, the molar absorption coefficient for either component separately is plotted logarithmically against wave length. The maximum absorption of the molecular compound (Figs. 2 and 3) is at 510 mμ. Here the contribution, to the density, of the free components is negligible and no correction is required. For all wave lengths > 450 mμ, the optical density of the mixture (Figs. 2 and 3) is solely due to the molecular compound. This optical density is shown in Fig. 2 to be proportional to the concentration of tetrachloroquinone, and, in Fig. 3, to be proportional to the product of the two concentrations if both are varied.

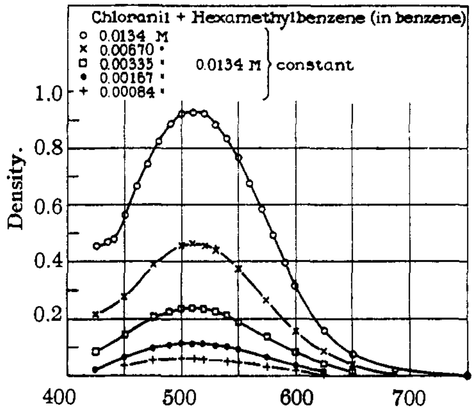

Fig. 2.

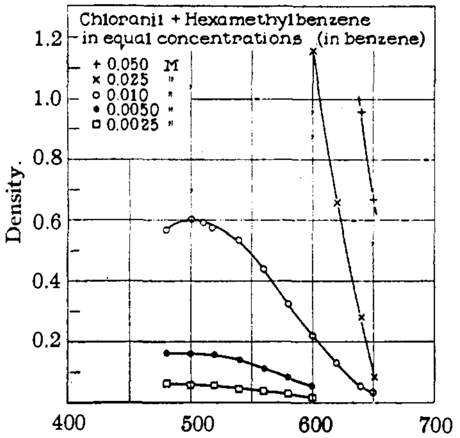

Fig. 3.

(b) Quinone + Hydroquinone.—The molar absorption coefficients are plotted, logarithmically, in Fig. 4, for the components singly. That part which is most important for this problem, in the violet region of the visible spectrum, is shown on a larger scale for quinone (not logarithmically) in Fig. 5. The molar absorption coefficient of quinone at its maximum around 430 mμ is 17 to 19.8 according to the solvent. Since the peak of absorption for quinone and for quinhydrone lie almost at the same wave length, the correction for the effect of quinone is always necessary. Although this correction is small in general, subtraction of the density due to the total quinone, instead of the uncombined quinone only, may cause a slight error. The effect of quinone is eliminated in Figs. 7 and 8, by taking as a blank a quinone solution of the same concentration but without hydroquinone. On the other hand, in Fig. 6, the

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[5] H. H. Cary and A. O. Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

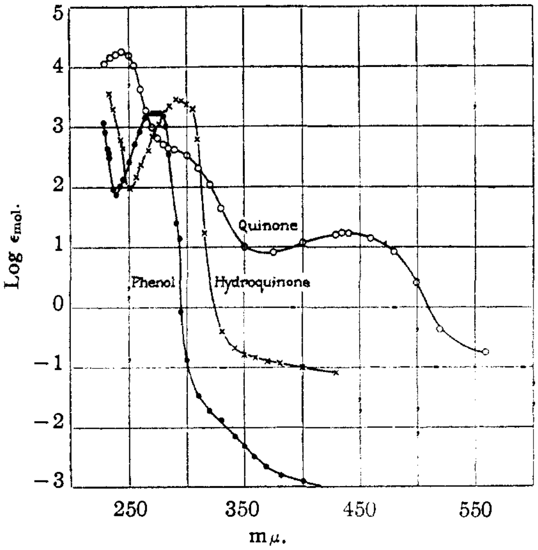

Fig. 4.

effect of quinone is eliminated by calculation, using the molar absorption coefficient of quinone according to the original data from which Fig. 5 was derived. In the three

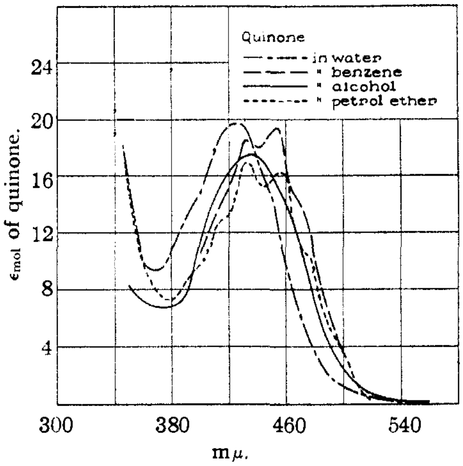

Fig. 5.

experiments ⊙, x and +, in Fig. 6, there is a relatively large, constant concentration of hydroquinone, and a low, varied concentration of quinone. Here the optical density is proportional to the quinone concentration. In experiment ●, an equimolar concentration of both components is used. Considering the fact that for the latter experiment the quinone correction is unusually great, involving a larger uncertainty, it can be stated that in all four experiments of Fig. 6 the density is proportional to the product of the concentrations of the two components, within the limits of error. The fact that this is true whether hydroquinone is nearly at the same concentration as quinone, or in excess, is important with reference to an observation made by other authors which will be discussed presently.

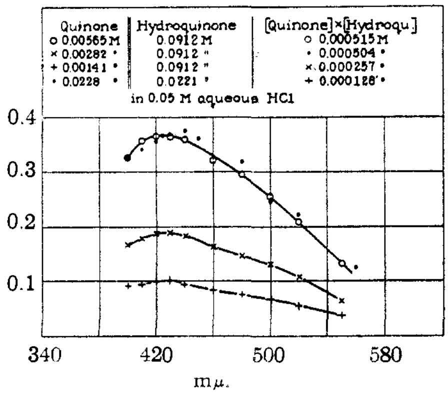

Fig. 6.

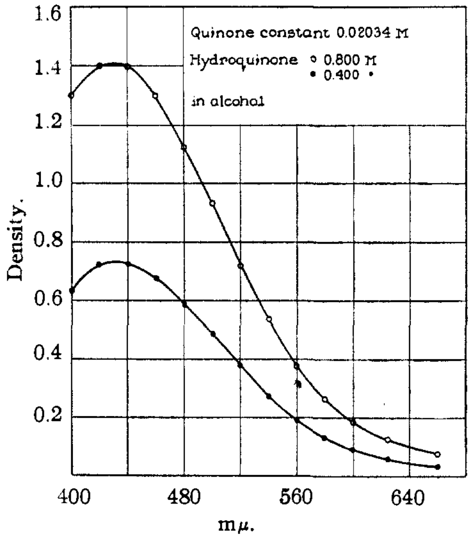

Fig. 7.

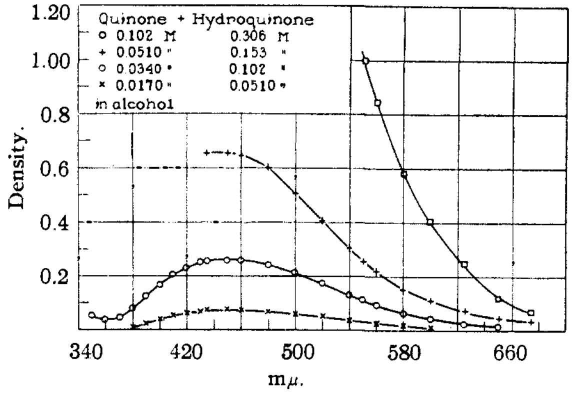

Fig. 8.

These experiments show also that the colored compound is not a free semiquinone radical. If it were so, the density would be proportional to $\sqrt{qb}$. It is in agreement with the authors' previous results[6] that no measurable amount of semiquinone radical is in equilibrium with the molecular compound (which may be considered as a dimerized radical) unless the solution is strongly alkaline, as has been shown for a solution of duroquinone + durohydroquinone.

These results are in part at variance with those published by Wagner and Grünewald,[7] the only authors, to the writers' knowledge, who have used spectrophotometry in the study of such problems, and then only for aqueous solutions of quinone + hydroquinone. They did not establish a continuous absorption curve nor locate the

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(6) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granick, THIS JOURNAL, **60**, 1678 (1938).

(7) C. Wagner and K. Grünewald, *Z. Elektrochem.*, **46**, 265 (1940).

maximum absorption but measured the optical density of aqueous solutions only at the wave length of three mercury lines. In equimolar mixtures of the components, the optical density was approximately proportional to the product of the two concentrations. On the ground of the small deviations from proportionality they calculated the dissociation constant of quinhydrone, which, however, they could not corroborate with measurements on mixtures with excess of hydroquinone. They refrain from making a decision as to whether this was due to some unknown optical effect or to the establishment of a compound different from Q_1B_1, say Q_1B_2. They agree with the writers that there is no measurable amount of semiquinone radical in equilibrium with the molecular compound. It can be seen that the present results do not coincide with those of the earlier authors' in several respects.

(c) **Duroquinone + Durohydroquinone.**—In one of the previous papers in this series (5) it was claimed that duroquinone + durohydroquinone do not combine to form any quinhydrone-like compound. This statement must be revised. To be sure, a mixture of the two substances in 20% pyridine or alcohol + 80% water, does not produce any precipitate, yet a very slight intensification of the color, compared with that of duroquinone alone, takes place. The steric hindrance for the formation of a quinhydrone due to the methylation at the ring is very conspicuous indeed, but it is not quite complete. Under proper conditions even a solid crystalline quinhydrone can be prepared. On dissolving equivalent amounts of either component at a high concentration in acetone, mixing both, and adding water slowly, a brownish precipitate arises, consisting of long, rod-shaped crystals, dichroitic blue and yellow. The dissociation of this quinhydrone in solution is extremely great. Judging from the appearance of color in a test-tube experiment, when a mixture of quinone + hydroquinone is compared with that of duroquinone + durohydroquinone at the same conditions, the dissociation of the latter is very much greater indeed. However, accurate spectrophotometric measurements cannot be carried out because durohydroquinone is so highly autoxidizable that the readings of the optical density rapidly change during the period of time necessary for an experiment.

Previous magnetic measurements[6,8] did not reveal any polymerization of the semiquinone radical of duroquinone as it arises in strongly alkaline solution. However, the crystalline, solid duroquinhydrone obtained as just described, from a non-alkaline solution, is diamagnetic. The susceptibility was measured with the method previously described[9] and found to be $= -140 \times 10^{-6}$ c.g.s.u., per equivalent (or half a mole). It is expected to be -124×10^{-6} according to Pascal's rules, on the assumption that the susceptibility of durohydroquinone is suitable for comparison. Considering the fact that this is just one single measurement and that the finely ground duroquinhydrone is a remarkably fluffy powder which can be packed homogeneously into the cylindrical vessel only with difficulty, the agreement is satisfactory. There is decidedly no paramagnetic semiquinone radical component in the crystals. The crystalline state, just as for the aromatic diamines,[9] is entirely in one of the two possible magnetic states, either fully diamagnetic or fully paramagnetic. This compound is fully diamagnetic. The previous magnetic measurements with the free radical in the dissolved state did not reveal any dimerization of the paramagnetic radical because they were carried out at *p*H 12, where the radical has the composition, $[OC_6(CH_3)_4O]^-$, but in the present investigations the solutions were neutral and so the radical has the composition $HOC_6(CH_3)_4O$, which is utterly unstable due to lack of equivalent resonance and which exists only, if at all, as the dimeric, diamagnetic quinhydrone with the H atom acting as a hydrogen bond involving dimeric resonance.[9] It may be added that in the meantime also the free radical, as a sodium salt, has been prepared in the solid state. In agreement with expectation, it is paramagnetic, however not to the full extent expected due to the fact that the solid preparation was not pure nor homogeneous.

(d) **Quinone + Resorcinol.**—The compound quinone + resorcinol is listed in Pfeiffer's book[1] among the compounds of composition Q_2B_1, according to indirect evidence presented by Kremann and associates.[2] These authors did not succeed in preparing the solid compound. It is however easy to prepare the intensely red, crystalline compound by mixing solutions of the components in acetone. One sample was prepared by mixing 1 g. of quinone (in 4 cc. acetone) with 1 g. of resorcinol (in 2 cc. of acetone), whereby the crystalline compound is obtained directly in pure form. Another preparation was obtained by mixing 0.4 g. of resorcinol (in 0.5 cc. of acetone) and a large excess of quinone, 1 g. (in 4 cc. of acetone). After slight evaporation of acetone, crystals of the free quinone are obtained. After addition of benzene the quinone dissolves and gradually brown crystals appear. Both samples of the quinhydrone were of the accurate composition, Q_1B_1. The analysis for quinone was made by dissolving the crystals in a little alcohol, diluting with water and titrating with titanous chloride. The stock solution of the latter diluted with a suitable volume of 6 *N* hydrochloric acid was standardized against quinone with methylene blue as internal indicator. It was ascertained that addition of resorcinol to a solution of quinone does not disturb the titration of quinone. So, the crystalline compound always has the composition Q_1B_1.

The spectrophotometric analysis of the solution containing quinone and resorcinol shows (Fig. 9 and Table I) that the optical density is proportional to the quinone concentration and also to the resorcinol concentration. The maximum absorption is at 370 mμ.

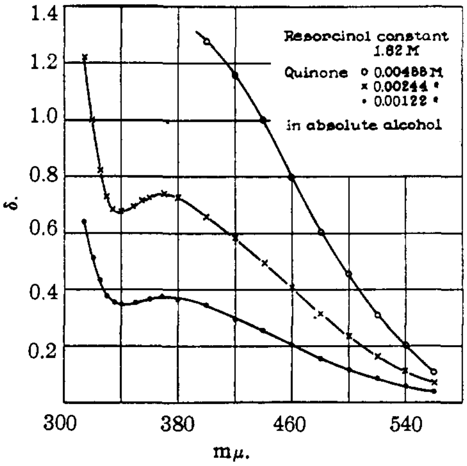

Fig. 9.

2. Examples of Compounds Having the Composition Q_1B_2 in the Solid State

(a) **Quinone + Phenol.**—First of all it was ascertained that solid "phenoquinone" has always the composition Q_1B_2 even when prepared from a solution, in petrolic ether, with a large excess of quinone. The analysis for quinone was made in the same manner as just described. The color of "phenoquinone" in solution is yellow, and the peak of absorption is not in the visible spectrum, but at 320 mμ. In Fig. 10 (disregarding for the time being the experiment marked △), it is shown that in alcoholic solution the optical density is proportional to the quinone concentration if the phenol concentration is kept constant. The same is true in petrol ether solution (Fig. 11). In Fig. 12 it is shown that on varying only the phenol concentration the density is proportional to the latter. So, in Fig. 12 the densities, corrected for the effect of both free components, for instance at 450 mμ, in the four experiments plotted, are in the ratio, 5.88:4.02:2.00:1.00, while the ratios of the phenol concentrations are, 6.1:4.0:2.00:1.00.

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(8) L. Michaelis, THIS JOURNAL, **63**, 2446 (1941).

(9) L. Michaelis and S. Granick, *ibid.*, **65**, 1747 (1943).

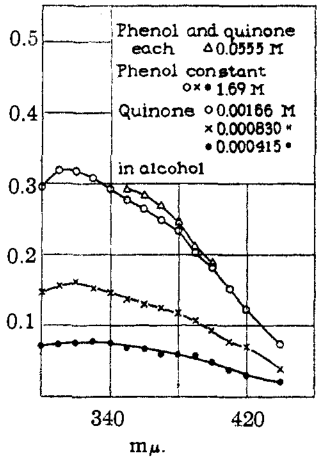

Fig. 10.

In these experiments although the concentrations have been varied, there is always an excess of phenol with respect to quinone. It is important to show that the same result is obtained when there is no excess of phenol. Only if this is true can one be sure that the reaction involved is always $Q + B \rightleftharpoons Q_1B_1$ and that another reaction, $Q_1B_1 + B \rightleftharpoons Q_1B_2$, does not occur. Such an experiment is shown in Fig. 10, marked △, where the concentration ratio is 1:1.

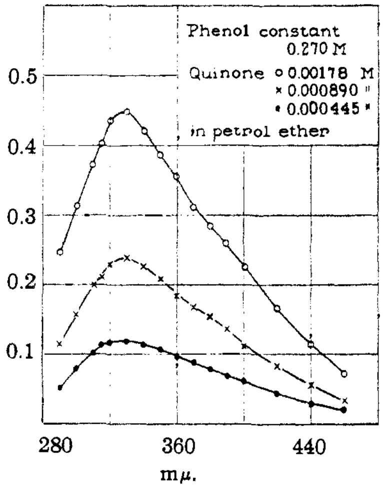

Fig. 11.

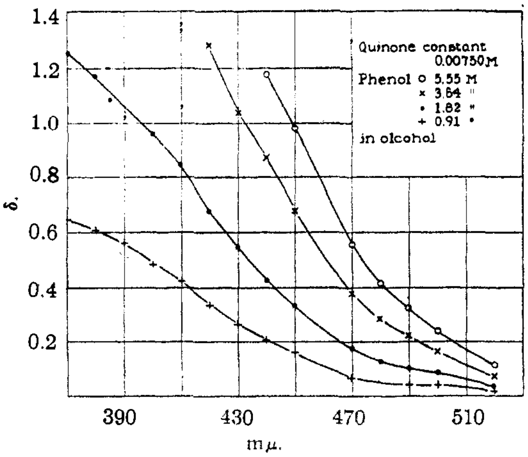

Fig. 12.

TABLE I

Q-Component and its molar concentration	B-Component and its molar concentration	Solvent	Wave length mμ at maximum absorption	δ	$\delta/qb = \epsilon_{st}$
Chloranil	Hexamethylbenzene				
0.0134				0.921	512
.00670	all			.468	520
.00335		Benzene	512	.239	530
.00167	0.0134			.116	515
.00084				.61	540
Quinone	Hydroquinone				
0.00565	0.0912	Water (0.05 *M* HCl)	425	.345	670
.00282	.0912			.181	705
.00141	.0912			.097	730
.0228	.0221			.37	720
.0203	.800	Alcohol	430	1.40	86
.0203	.400			0.72	89
Quinone	Methylhydroquinone				
0.000167	4.15			.60	86
.0000875	4.15	Alcohol	420	.284	82
.0000417	4.15			.143	83
.00176	3.67			.463	72
.00176	1.22			.171	80
Quinone	Dimethylhydroquinone				
0.0200	0.250			.501	100
.0200	.125	Alcohol	410	.252	101
.0200	.0625			.131	105
Quinone	Diethylhydroquinone				
all 0.0203	0.171			.357	100
	.0855	Alcohol	420	.181	104
	.0427			.089	90
all 0.0222	.400			.509	57
	.200	Benzene	420	.268	60
	.100			.145	65
Quinone	Phenol				
0.00166	all			0.321	114
.000830	1.69	Alcohol	320	.165	117
.000415				.085	122
.00178	all	Petrol ether		.446	93
.000890	0.270		330	.237	99
.000445				.118	98
Quinone	Anisol				
all	2.34			1.084	163
	1.17	Alcohol	320	0.534	161
0.00284	0.585			.280	169
all	3.82			1.398	67
	1.91	Petrol ether	350	0.770	72
0.00550	0.955			.377	72
Quinone	Phenetól				
all	3.26	Petrol ether		1.301	76
	1.63		350	0:745	84
0.00525	0.815			.398	93
Quinone	Resorcinol				
0.00488	1.82			1.385	156
.00244	1.82	Alcohol	370	0.728	164
.00122	1.82			.374	169
.00534	1.81			1.361	141
.00534	0.905			0.754	156
Quinone	Phloroglucinol				
0.0274	0.238	Alcohol	420	0.124	190
.0137	.119			.031	190

The absorption due to free quinone is so strong here that the optical density due to the molecular compound can be measured only at wave lengths > 350 mμ, but not at the maximum of absorption at 320 mμ. On looking at the results, *e. g.*, at 360 mμ, the corrected density was found to be 0.284. This, divided by the product of the two concentrations, yields $\epsilon_{st} = 92$. For the same wave length, the other experiments gave values ranging from 92 to 96, a satisfactory agreement.

(b) **Quinone + Hydroquinone Monomethyl Ether.**—The composition of the crystalline compound, a long time ago,[10] was found to be Q_1B_2. This can be easily confirmed by the method of analysis just described. For the dissolved state, however, it is shown (Table I) that the optical density of the mixture is proportional, at constant concentration of the hydroquinone ether, to the concentration of quinone. The maximum of absorption is at 420 mμ, very close to that of quinone + hydroquinone, and very far from that of phenol + quinone which is at 320 mμ. In Table I the density is shown to be proportional also to the concentration of hydroquinone monomethyl ether. So, the composition in solution is Q_1B_1.

3. Example for a Case Where the Solid Compound is Q_2B_1

Among the tri-hydroxybenzenes only phloroglucinol combines with quinone to form a crystalline compound stable enough to allow an analysis both in the solid and in the dissolved states. The solid compound is perfectly stable, the solution at least stable enough to permit of spectrophotometry with freshly prepared solutions. The crystalline compound has always the composition Q_2B_1, a composition which has heretofore not been known, nor even expected. One sample was prepared by mixing 1 g. of quinone (in 4 cc. of acetone) with 1.1 g. of phloroglucinol (in 2 cc. of acetone). Crystallization proceeds slowly but copiously. Another sample was prepared with an excess of quinone, by mixing 1.5 g. of quinone (in 6 cc. of acetone) with 0.5 g. of phloroglucinol (in 1 cc. of acetone). This mixture yields directly only quinone crystals. After adding an equal volume of benzene and slight evaporation at room temperature the red-brown quinhydrone crystals appear. Both samples of the solid quinhydrone, when titrated with titanous chloride, were found to have accurately the composition Q_2B_1.

A mixture of the two components in alcohol shows the formation of a brownish compound with maximum absorption at 420 mμ, close to that of quinone + hydroquinone, and very different from quinone + resorcinol (360 mμ). Freshly prepared alcoholic solutions gave the results presented in Table I. In another experiment, in which only the quinone concentration was varied, the optical density was proportional to that concentration, within the limits of error. So, the optical density due to the molecular compound is proportional to the product of the concentrations of the two components, hence its composition in the dissolved state is Q_1B_1.

4. Examples of Molecular Compounds Which do not Exist in the Solid State

(a) **Quinone + Hydroquinone Dimethyl Ether.**—No molecular compound of phenol + hydroquinone dimethyl ether has been obtained. However, a remarkable phenomenon can be observed in this case, which throws much light on the difference in behavior in the solid and in the liquid state. When a mixture of solid phenol and dimethylhydroquinone is melted, an intensely red liquid is obtained which remains so, even after supercooling. As crystallization sets in, all the red color disappears. The solid material is yellow and consists of two kinds of crystals, the light yellow ones of quinone and the colorless ones of hydroquinone dimethyl ether. This process is reversible. In alcoholic solution a mixture of quinone + dimethylhydroquinone shows an orange color, very much more intense than that of quinone alone, and here again the absorption due to this strongly colored substance is proportional both to the concentration of quinone and, as shown in Table I, to that of dimethylhydroquinone, so, the composition of the colored compound is Q_1B_1, but this compound exists only in solution.

The absorption maximum of this molecular compound in alcohol solution is, at 410 mμ, close to but not quite equal to that of quinhydrone.

(b) **Quinone + Hydroquinone Diethyl Ether.**—This case is quite analogous in every respect to that of the dimethyl ether. The larger volume of the ethyl group, as compared with the volume of the methyl group, does not influence the properties of the molecular compound. Table I shows the values both for alcohol and for benzene solutions.

(c) **Quinone + Anisole.**—No crystalline molecular compound of quinone and anisole can be prepared. In solution, however, such a compound does exist to a slight extent. When a solution of quinone, in alcohol or in petrol ether is mixed with anisole, the color is intensified. The maximum absorption of the compound in alcohol is at 320 mμ (Table I), just as for phenoquinone, and at 350 mμ in petrol ether. Here again the absorption due to the molecular compound is very much stronger than that of quinone alone, and the optical density is rather accurately proportional to the concentration of anisole. So, the molecular compound again is Q_1B_1.

(d) **Quinone + Phenetol.**—The result is similar to that obtained in the preceding case.

Significance of the ϵ_{st}, the Standard Absorption Coefficient

Since the optical density due to the molecular compound must be

$$\delta = \epsilon_{mol} \times m$$

where ϵ_{mol} is the molar absorption coefficient of the compound and m is its concentration, one obtains from equation 1

$$\epsilon_{st} = \epsilon_{mol} \times k$$

where k is the association constant.

There is good reason to assume that the molar absorption coefficient of any one substance is nearly independent of the solvent. Whenever a considerable variation of the molar absorption coefficient of any dye in different solvents is encountered, it can be always attributed to a change in chemical structure, say, a change of a quinonoid–lactoid equilibrium, or a different state of molecular aggregation, according to the solvent. There is no reason to assume that the molar absorption coefficients of molecular compounds of composition Q_1B_1 should vary appreciably according to the solvent. Consequently, the values of ϵ_{st} for any one compound in different solvents may be considered approximately as relative values of the association constant of that compound in various solvents. For instance, Table I shows that the association constant of quinone + hydroquinone is about eight times greater in water than in alcohol, probably due to the fact that in the competition among the affinities of the components for the solvent and for each other, the association is more inhibited by alcohol than by water.

On the other hand, on comparing the various values of ϵ_{st} for a series of molecular compounds in the same solvent, it is not possible, in general,

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[10] H. Wichelhaus, *Ber.*, **12**, 1501 (1879): for the correction of his result, see O. Hesse, *Ann.*, **200**, 254 (1880).

to decide whether the variation is due to a change of ϵ_{mol}, or of k, or of both. However, on comparing a homologous series, such as the compounds of quinone and, on the other hand, either hydroquinone or its ethers, in the same solvent, the values of ϵ_{st} are found to vary but little within this homologous series. It does not seem probable that the variation of ϵ_{mol} should be always just inversely proportional to the variation of k. It may rather be inferred from this fact, with high probability, that both ϵ_{mol} and k are approximately constant within the homologous series. For instance, both the molar absorption coefficients and hence the association constants are found to be almost alike for the compounds formed by quinone either with hydroquinone, its monoether, or its di-ethers, in alcohol. The substitution in the OH group is no steric hindrance to the formation of the molecular compound in solution.

In benzene the situation is slightly different. Quinone + hydroquinone cannot be compared with the other compounds of quinone because in benzene even at extremely low concentration precipitation of crystalline quinhydrone occurs. However, the compounds of quinone with the various ethers of hydroquinone can be mixed at proper concentration without any precipitation occurring. It can be seen that ϵ_{st} for the monomethyl ether compound is about twice that for a di-alkyl ether compound. In all probability this is due, not to any appreciable change of ϵ_{mol}, but to a slight change in the association constant, k, which in its turn is probably due to competition between the mutual affinity of the components and the affinity between components and solvent.

Summary

Highly colored molecular compounds of the quinhydrone type exist, not only in the crystalline state, but, to a slight extent, also in solution, in equilibrium with their free components. Because of their intense color such compounds lend themselves to a study by spectrophotometric methods. The compounds studied here consist usually of a quinone (Q) and another component of benzenoid structure (B), usually a phenolic compound. In the crystalline state the stoichiometric composition of the compound may vary, according to the particular phenolic compound used. It may be Q_1B_1, Q_1B_2, or Q_2B_1. No solid compound is formed when the OH group of phenol, or all OH groups in a poly-phenol, are alkylated. In the dissolved state, however, all of these compounds have the composition Q_1B_1, and molecular compounds exist just as well with unsubstituted as with alkylated phenols. This conclusion is based on the fact that the absorption of light due to the molecular compound is always proportional to the concentration of either component. It is furthermore shown that the affinity of quinone for a phenolic compound in solution is not essentially altered by alkylation of the phenolic OH groups. It is inferred from this that in the dissolved state the rings of the two components are superimposed upon each other and are not coplanar, and that no hydrogen bond plays any essential role in the establishment of these compounds. The crystalline compounds may differ from the dissolved ones, both in their stoichiometrical composition and in their spatial structure.

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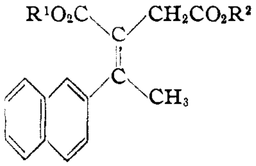
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

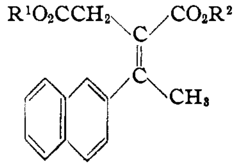
The Condensation of 2-Acetylnaphthalene with Diethyl Succinate[1]

BY WILLIAM S. JOHNSON AND ARTHUR GOLDMAN

In the course of certain synthetic work being carried out in this laboratory the occasion arose to investigate the condensation of 2-acetylnaphthalene with diethyl succinate. Through the efforts of Stobbe and his collaborators it has been well established that the alkoxide-catalyzed reaction of succinic ester with a ketone proceeds not by the acetoacetic ester type but mainly by an aldol type of condensation between the carbonyl group of the ketone and a methylene group of the ester. Stobbe and Lenzner[2] have reported that this condensation with 2-acetylnaphthalene gave a crystalline half-ester, m. p. 103–104° (yield unspecified). Saponification yielded a dicarboxylic acid, m. p. 165° (dec.), which they presumed to be an itaconic acid (formula I or II) by analogy with the products formed in similar condensations.[3]



I ($R^1 = R^2 = H$)
Ia ($R^1 = C_2H_5$, $R^2 = H$)
Ib ($R^1 = H$, $R^2 = C_2H_5$)
Ic ($R^1 = R^2 = C_2H_5$)



II ($R^1 = R^2 = H$)
IIa ($R^1 = H$, $R^2 = C_2H_5$)
IIb ($R^1 = C_2H_5$, $R^2 = H$)
IIc ($R^1 = R^2 = C_2H_5$)

In the present investigation when the condensation was conducted in ether solution with alcohol-free sodium ethoxide according to the reported

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(2) Stobbe and Lenzner, *Ann.*, **380**, 93 (1911).

(3) *Cf.* the reaction with acetophenone: (a) Stobbe, *Ann.*, **308**, 114 (1899); (b) *Ber.*, **37**, 1619 (1904); (c) *Ann.*, **380**, 36 (1911).