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Interconversion by Hydrogen Transfer of Unsymmetrically Substituted Quinhydrones in the Solid State. Crystal Structure of the 1:2 Complex of 2,5-Dimethylbenzoquinone with Hydroquinone

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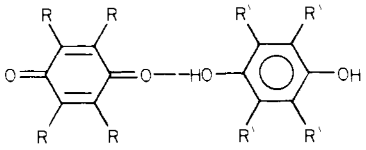
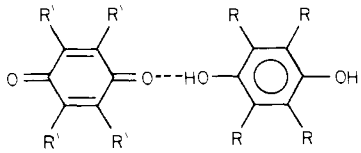
Abstract: Crystalline quinhydrones, prepared by grinding together a solid quinone and hydroquinone, have been found to undergo a thermal self-oxidation–reduction on heating or even on standing at room temperature. For example, the 1:1 complex benzoquinone/naphthohydroquinone has been found to rearrange to the 1:1 complex naphthoquinone/hydroquinone and the 1:1 complex phenylbenzoquinone/naphthohydroquinone to naphthoquinone/phenylhydroquinone (1:1) when heated at 80 °C. FTIR and X-ray powder photography show that the products are microcrystalline and have the same crystal structures as those same products prepared directly from the components by grinding the solids together or by crystallization from solution. The 1:1 complex benzoquinone/2,5-dimethylhydroquinone, on the other hand, rearranges in the solid state to a complex of 2,5-dimethylbenzoquinone with 1,4-hydroquinone in a ratio of 1:2—the extra molecule of 2,5-dimethylbenzoquinone being eliminated. 2,5-Dimethylbenzoquinone and 1,4-hydroquinone form the same 1:2 complex either when ground together in the solid state or when the complex is crystallized from toluene–methanol. Crystallization from benzene gives a complex in which some of the hydroquinone molecules of the 1:2 complex above appear to have been replaced by benzene molecules. Similarly benzoquinone/2-methylhydroquinone (1:1) forms 2-methylbenzoquinone/hydroquinone (ratio 1:2) when heated or on standing. Preparation of the product complex by crystallization gives a somewhat variable ratio of quinone to hydroquinone ranging from 1:1.5 to 1:2. Crystallization from benzene gives a complex with some incorporation of benzene. The crystal structure of the 1:2 complex 2,5-dimethylbenzoquinone/hydroquinone has been determined. The structure is triclinic, $P\bar{1}$, with a = 7.683 (1) Å, b = 9.758 (2) Å, c = 6.050 (1) Å, α = 103.62 (2)°, β = 91.58 (2)°, γ = 89.17 (2)°, and Z = 1, $C_8H_8O_2 \cdot 2C_6H_6O_2$. The structure has been determined by direct methods and refined to R 0.039 for the 1538 reflections recorded with an automatic single-crystal diffractometer.

Solid complexes of quinones with hydroquinones have long attracted attention because of their deep colors and the structural problem they have presented.[1] They are largely dissociated in solution. When the quinone and hydroquinone bear different substituents the quinhydrones thus formed have been shown to be quite stable in the solid state but to undergo a rapid redox equilibration in solution. In the earliest examples reported, the quinone and hydroquinone differed by isotopic substitution. Thus, Brodskii and Gragerov[2] had prepared the quinhydrone **1a** with a single ring labeled with deuterium and showed that, although in the crystalline state it was stable at room temperature, it underwent slow conversion to **2a** at 70 °C.



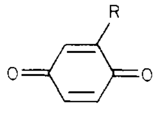
1a, R = H; R' = D
b, R = CH_3; R' = $^{14}CH_3$



2a, R = H; R' = D
b, R = CH_3; R' = $^{14}CH_3$

In an independent investigation[3] Bothner-by showed that the isomeric quinhydrones **1b** and **2b** from tetramethylbenzoquinone and tetramethylhydroquinone and its redox isomer labeled in the methyl groups with ^{14}C were stable in the solid state but readily interconverted in solution.

In a study by Desiraju, Curtin, and Paul,[4] isomeric complexes differing in the chemical nature of their substituents could be prepared from the unsymmetrically substituted pairs **3c**/**4d** and **3d**/**4c** only by rapid crystallization from a solvent; although they were found to undergo interconversion rapidly in solution, they were quite stable in the solid state and, in fact, at that time had not been induced to undergo interconversion in the solid state. This paper describes the pursuit of quinhydrones sufficiently reactive to undergo such a redox reaction in the solid state.



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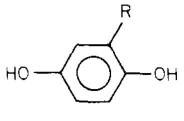

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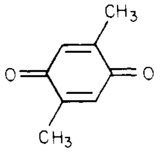

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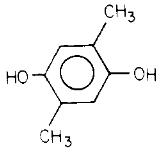

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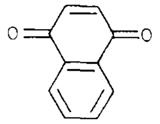
a, R = H; b, R = CH_3; c, R = C_6H_5; d, R = p-ClC_6H_4



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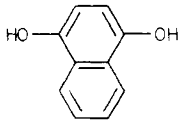

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The reactions mentioned above are thermochemically approximately balanced, and it seemed likely that if we could prepare

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(1) (a) Bernstein, J.; Cohen, M. D.; Leiserowitz, L. "The Chemistry of the Quinonoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; Chapter 2, "The Structural Chemistry of Quinones", (b) Foster, R.; Foreman, M. I. "The Chemistry of Quinonoid Compounds"; Patai, S.; Ed.; Wiley: New York, 1974; Chapter 6, "Quinone Complexes".

(2) Brodskii, A. I.; Gragerov, I. P. *Dokl. Akad. Nauk SSSR* **1951**, *79*, 277–279.

(3) (a) Bothner-by, A. A. *J. Am. Chem. Soc.* **1951**, *73*, 4228–4230; (b) *Ibid.* **1953**, *75*, 728–730.

(4) Desiraju, G. R.; Curtin, D. Y.; Paul, I. C. *J. Org. Chem.* **1977**, *42*, 4071–4075.

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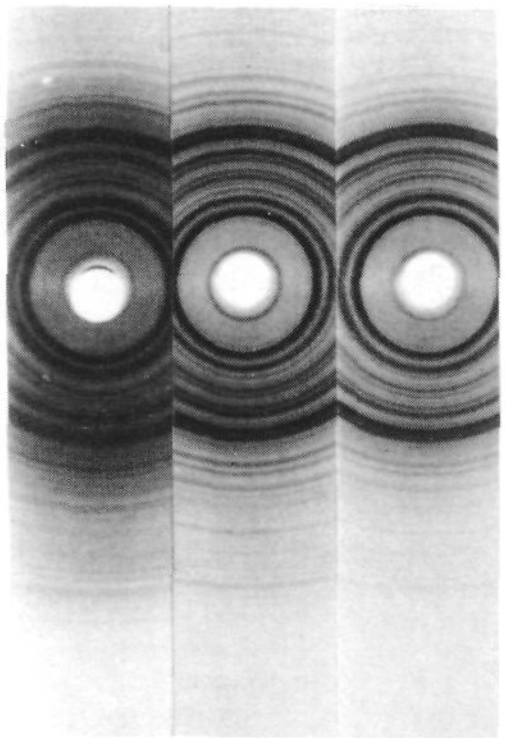

Figure 1. X-ray powder photographs of (left) the unstable quinhydrone from benzoquinone (**3a**) and naphthohydroquinone (**8**) prepared by grinding the components together, (center) the stable complex of naphthoquinone (**7**) and hydroquinone (**4a**) formed by heating the above unstable complex, and (right) the complex from **7** and **4a** prepared by crystallization from solution.

complexes whose redox rearrangement involved a larger free energy change the solid-state reaction might be induced to occur more readily. However, if the quinhydrones are to have the desired reactivity in the solid state, they are likely to be prohibitively reactive in the solution from which they would customarily be formed.

In a recent investigation[5] we have resolved this synthetic problem by utilization of a solid-solid reaction. Thus the synthesis of unsymmetrically substituted quinhydrones formed by grinding together a quinone such as **3**, **5**, or **7** and a hydroquinone such as **4**, **6**, or **8** leads to complex formation without any detectable redox rearrangement of the isomeric quinhydrone.

The present paper describes our exploration of several solid-state redox reactions and the discovery of sometimes unexpected control of the outcome of the reaction by crystal energies.

Experimental Section

Fourier transform infrared spectra were obtained with a Nicolet 7000 FTIR spectrophotometer. Differential calorimetry scans were recorded with a Du Pont 900 Thermal Analyzer. DSC temperatures reported are extrapolated onset values.

Rearrangement of Benzoquinone/Naphthohydroquinone (3a/8) to Naphthoquinone/Hydroquinone (7/4a). The complex (**3a/8**) was prepared by grinding the solids together as discussed in a previous paper.[5a] Rearrangement could be carried out by heating a sample of the complex in a glass capillary tube (id 0.7 mm) in an oil bath at 80–85 °C for 10 h or even on prolonged standing at room temperature; there was a pronounced color change from the blue-black of the starting complex to reddish-blue of the product. An X-ray powder photograph taken before reaction was quite different from one taken afterward (Figure 1); the latter photograph was identical with that of the 1:1 complex of naphthoquinone with hydroquinone (**7/4a**) prepared either by grinding of the solids together or by crystallization from a solvent. The most informative method of following the reaction was with the FTIR (Figure 2); the spectrum of the initial solid (Nujol mull) was markedly different from that of the product. Thus, when a sample of complex **3a/8** was heated at 70–80 °C for 8 h, absorption due to the carbonyl groups of the complexed benzoquinone at 1661 and 1632 cm^{-1} decreased in intensity, and there developed a sharp carbonyl absorption at 1646 cm^{-1} (with a small shoulder at 1630 cm^{-1}). The triangular hydroxyl O–H stretching absorption characteristic of the hydrogen-bonded unit in quinhydrones was very similar in each complex. Other absorptions at 1588, 1240, 1220, 950, and 875 cm^{-1} disappeared and new absorptions at 1230 and 850 cm^{-1} appeared during the reaction. The spectrum of the product was identical with that of the complex **7/4a** prepared by crystallization from a solvent. A series of spectra obtained from samples removed during the course of a reaction were compared with artificial mixtures of complex **3a/8** with **7/4a** in the ratio of 25:75, 50:50, and 75:25, as well as spectra of authentic samples of those complexes which might have accumulated as intermediates formed by disproportionation. There was no indication of such disproportionation as shown by the absence from the samples taken during reaction of absorptions at 841, 807, and 752 cm^{-1} characteristic of complex **7/8** and of absorptions at 980 and 835 cm^{-1} found in the monoclinic and triclinic quinhydrones **3a/4a**. Differential scanning calorimetry showed when a sample was heated at 10 °C/min a small broad exotherm between 60 and 100 °C and a larger, sharp endotherm at 121 °C. The product **7/4a** showed only a sharp endotherm at 125 °C. Equimolar mixtures of the two complexes **3a/8** and **7/4a** when ground together for 20 min and heated for 7 h at 80–85 °C also gave the complex **7/4a** as shown by the single endotherm at 125 °C in the DSC and by the similarity of the IR spectrum of the product to those of other preparations of this complex. Similarly an equimolar mixture of benzoquinone, naphthoquinone, hydrobenzoquinone, and hydronaphthoquinone ground together for 20 min and heated at 80–85 °C for 7 h gave the DSC and FTIR expected for the complex **7/4a**.

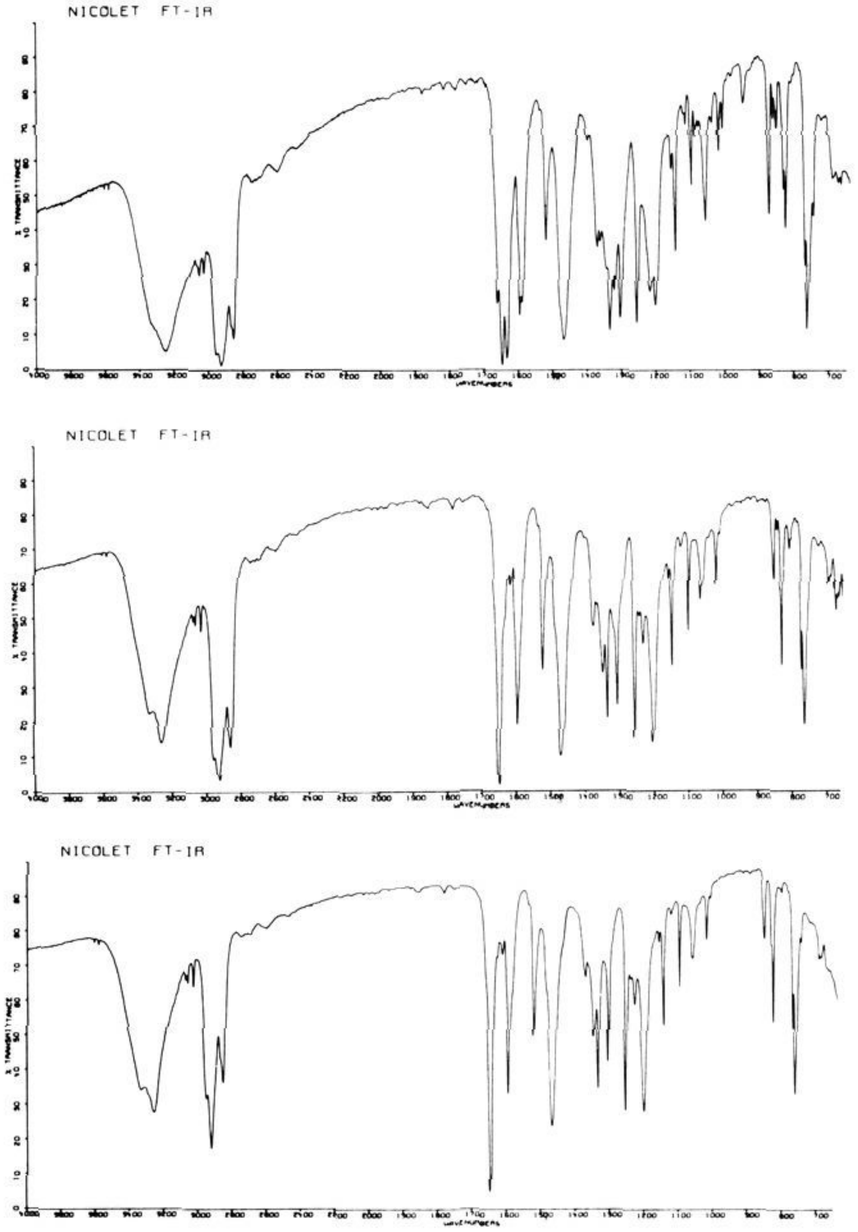

Figure 2. FTIR spectra: (Top) The 1:1 complex from benzoquinone (**3a**) and naphthohydroquinone (**8**) prepared by grinding. (Middle) The complex prepared by heating the above-mentioned 1:1 complex. (Bottom) The complex prepared by crystallizing a mixture of naphthoquinone (**7**) and hydroquinone (**4a**). The two lower spectra are identical.

Effect of Nujol on the Rate of Solid-State Rearrangement of 3a/8 to 7/4a. During the determination of the FTIR spectra (as Nujol mulls) it was observed that the redox rearrangement reaction was markedly accelerated in the Nujol suspension, particularly in the FTIR instrument where the repeated scans needed for a high-resolution spectrum were likely to lead to indications in the spectrum of the formation of the rearrangement product. In Nujol even without exposure to the laser beam of the FTIR instrument it was found that rearrangement was substantially accelerated in comparison to reaction in the solid state. The FTIR spectrum of a sample that had stood for 1 h suspended in Nujol resembled that of a sample that had stood for 24 h in the solid state.

Rearrangement of Phenylbenzoquinone/Hydronaphthoquinone (3c/8) to Naphthoquinone/Phenylhydrobenzoquinone (7/4c). The blue-black

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[5] (a) Patil, A. O.; Curtin, D. Y.; Paul, I. C., *J. Am. Chem. Soc.* **1984**, *106*, 348–353. (b) Patil, A. O.; Wilson, S. R.; Curtin, D. Y.; Paul, I. C. *J. Chem. Soc., Perkin Trans 2*, in press.

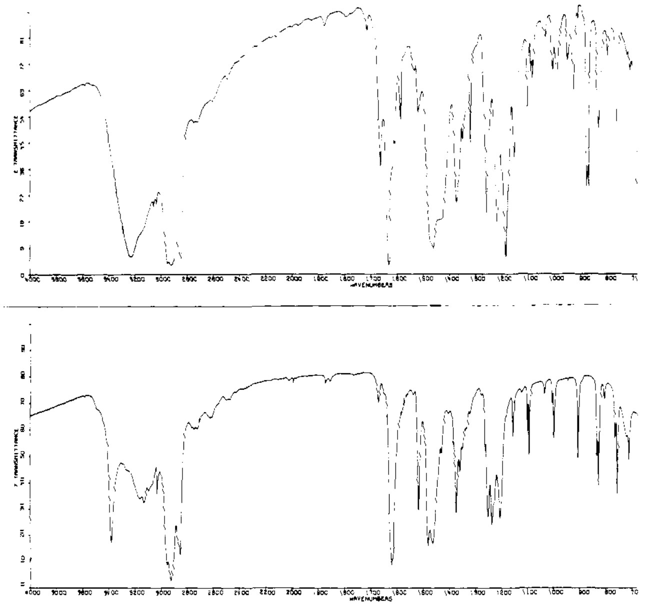

Figure 3. FTIR spectra: (Top) The 1:1 complex of benzoquinone (**3a**) and 2,5-dimethylhydroquinone (**6**) prepared by grinding the components together. (Bottom) The 1:2 complex of 2,5-dimethylbenzoquinone (**5**) and hydroquinone (**4a**) prepared by crystallization of the components.

complex **3c**/**8** when heated as above for 10 h at 80–85 °C changed to the reddish blue color of the complex **7**/**4c**. X-ray powder photography showed changes and the powder photograph of the product was identical with a powder photograph of the complex **7**/**4c** prepared by solid-solid reaction or by crystallization from a solvent. The DSC of a sample heated at 10 °C/min showed a small broad exotherm between 60 and 100 °C and a large sharp endotherm at 124 °C. The product **7**/**4c** showed only a sharp endotherm at 131 °C. The FTIR showed incompletely resolved multiplets in the carbonyl region (1629–1660 cm^{-1}), which changed during heating to a sharp carbonyl absorption at 1645 cm^{-1}, characteristic of the rearrangement product **7**/**4c**. Other absorptions at 1590, 1350, 1100, 1058, 1007, 829, and 825 cm^{-1} decreased in intensity during reaction while absorptions at 1528, 1496, 1200, 1075, 1064, and 813 cm^{-1} appeared.

Rearrangement of Benzoquinone/2,5-Dimethylhydroquinone (3a/6) to the 1:2 Complex 2,5-Dimethylbenzoquinone/Hydroquinone (5/4a). The color of the blackish blue 1:1 complex **3a**/**6** prepared by solid–solid reaction was found to change to reddish brown when heated in a melting capillary at 80–85 °C for 6–8 h or even on standing at room temperature. The FTIR (Figure 3) showed the disappearance of peaks at 3240, 1634, 1588, 1218, 1187, 1080, 950, 928, 877, 870, and 795 cm^{-1}, while new absorption peaks appeared at 3380, 3150, 1620, 1237, 1205, 908, 808, and 757 cm^{-1}. The FTIR of the product was found to be similar to that of the 1:2 complex **5**/**4a** prepared by crystallization from solution or by gel diffusion but with the additional peaks at 1665, 1640, 1350, 926, and 795 cm^{-1} indicative of the presence of some 2,5-dimethylbenzoquinone. The FTIR spectrum was, in fact, identical with that of an equimolar mixture of the 1:2 complex **5**/**4a** and dimethylquinone **5**. The DSC of the complex **3a**/**6** showed a small broad exotherm (70–100 C) followed by endotherms attributed to the melting of dimethylquinone (114 °C) and the 1:2 complex **5**/**4a** (152 °C). Complex **5**/**4a** prepared by crystallization from solution showed a sharp endotherm at 165 °C.

The complex **5**/**4a** prepared by crystallization from benzene/acetic acid (3:1) gave the expected ^{1}H NMR spectrum (Me$_2$SO-d_6) for the 1:2 complex with a small additional peak at δ 7.3 (0.5–1.0 protons). The same sample crystallized from toluene/methanol (3:1) showed no peaks attributable to solvent incorporation.

Rearrangement of Benzoquinone/Methylhydroquinone (3a/4b) to the 1:2 Complex Methylbenzoquinone/Hydroquinone (3b/4a). The blackish blue 1:1 complex **3a**/**4b** prepared by grinding the starting materials together was found on heating to 70–75 °C for 8–10 h or even on standing at room temperature to change to reddish brown. FTIR absorptions at 1635, 1590, 1500, and 1083 cm^{-1} diminished during the reaction while those at 3380, 1628, 1600, 1517, 1228, and 1095 cm^{-1} appeared. However, peaks at 945, 875, and 815 cm^{-1} failed to disappear completely even after the sample stood at room temperature for 50 days and was heated for 10 h at 65 °C. The FTIR of the sample after heating was found to be similar to that of the 1:2 complex **3b**/**4a** prepared by crystallization of the components from toluene/methanol or by gel diffusion. However, recrystallization from benzene gave a product with an extra peak at δ 7.3, corresponding to 0.5–1.0 proton. The DSC of complex **3a**/**4b** showed a small broad exotherm and two endotherms at 87 and 134 °C which can be attributed to the melting of methylquinone (**3a**) and the 1:2 complex **3b**/**4a**. Complex **3b**/**4a**, prepared by crystallization, showed a single sharp endotherm at 137 °C.

Table I. Final Atomic Coordinates in Fractions of the Unit Cell

	x	*y*	*z*
O(1)	0.7839 (1)	0.1115 (1)	0.7138 (2)
C(2)	0.8927 (2)	0.0542 (1)	0.8535 (2)
C(3)	0.9419 (2)	−0.0867 (2)	0.7967 (2)
C(4)	1.0496 (2)	−0.1411 (1)	0.9428 (2)
O(5)	0.7130 (2)	0.3764 (2)	0.6377 (3)
C(6)	0.8584 (2)	0.4362 (2)	0.5718 (3)
C(7)	1.0255 (3)	0.4094 (2)	0.6424 (3)
C(8)	1.1667 (3)	0.4726 (2)	0.5709 (3)
C(9)	0.5416 (2)	−0.1496 (2)	−0.0321 (2)
C(10)	0.5468 (2)	0.1054 (2)	0.1963 (2)
O(11)	0.6790 (2)	−0.0792 (1)	0.3296 (2)
C(12)	0.5946 (2)	−0.0432 (2)	0.1771 (2)
C(13)	0.5878 (3)	−0.2999 (2)	−0.0440 (4)
H(1)	0.758 (3)	0.044 (3)	0.574 (4)
H(3)	0.899 (2)	−0.144 (2)	0.661 (3)
H(4)	1.082 (2)	−0.239 (2)	0.905 (3)
H(5)	0.746 (3)	0.303 (3)	0.675 (4)
H(7)	1.043 (2)	0.346 (2)	0.734 (3)
H(8)	1.284 (3)	0.459 (2)	0.621 (4)
H(10)	0.590 (2)	0.173 (2)	0.342 (3)
H(131)	0.557 (4)	−0.356 (3)	−0.176 (5)
H(132)	0.541 (3)	−0.333 (2)	0.087 (4)
H(133)	0.714 (4)	−0.318 (3)	−0.037 (5)

Melting Point Behavior of Quinone/Hydroquinone Mixtures. Melting points were determined for a series of mixtures with ratios of quinone/hydroquinone of 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90. The naphthoquinone/hydroquinone pair showed a maximum at a composition of 50/50 (mp 124–126 °C). The dimethylbenzoquinone/hydroquinone pair showed a maximum at 33/67 (mp 165–166 °C). The methylquinone/hydroquinone pair showed a maximum at 40/60 (mp 136–138 °C).

Determination of the Crystal Structure of a 1:2 Complex of 2,5-Dimethylbenzoquinone with Hydroquinone (5/4a). Crystal data: C$_8$H$_8$O$_2$·2C$_6$H$_6$O$_2$, mol wt 356.4, triclinic, a = 7.683 (1) Å, b = 9.758 (2) Å, c = 6.050 (1) Å, α = 103.62 (2)°, β = 91.58 (2)°, γ = 89.17 (2)°, V = 440.7 (1) Å^3, ρ_{calcd} = 1.34 g/cm^3, Z = 1, space group $P\bar{1}$, μ(Mo Kα) = 0.71069 Å. Cell dimensions were obtained by a least-squares fit to the settings for 15 carefully centered reflections. The data (hkl and $\bar{h}\bar{k}l$) collected on a Syntex P2$_1$ diffractometer to 2θ = 55° (Mo Kα) gave 1538 independent reflections with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors but no absorption correction was made. Attempts to solve the structure with the program MULTAN 80 were unsuccessful. Application of the program RANTAN gave a promising solution but the E map had two images of the structure separated by a distance of the same order as the bond lengths (1.2–1.4 Å). The model obtained by averaging the positions of the non-hydrogen atoms in the two images provided a satisfactory trial structue for refinement. Least-squares refinement and difference-Fourier synthesis yielded the remainder of the structure. The final refinement cycles employed positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic temperature factors for the hydrogen atoms. The final values of R, R_w, and "goodness of fit" were 0.039, 0.044, and 1.94, respectively. The reflections were weighted as $1.0/(\sigma^2(F) + 0.0004F^2)$ and the scattering curves were taken from ref 6 and included the anomalous dispersion corrections. The highest peak on a final difference map was 0.25 e/Å^3. The final atomic coordinates are given in Table I. The temperature factors and structure factors are in the supplementary material.[7]

Results and Discussion

Measurements of reduction potentials of a variety of quinones by Conant and Fieser[8] and by Hunter and Kvalnes[9] proved to be

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(6) Ibers, J. A.; Hamilton, W. C. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV.

(7) See paragraph at end of paper regarding supplementary material.

(8) (a) Conant, J. B.; Fieser, L. F. *J. Am. Chem. Soc.* **1923**, *45*, 2194–2218; (b) *Ibid.* **1924**, *46*, 1858–1881.

Table II. Differences in Normal Reduction Potentials of Some Quinones

compound	redn pot.; V (EtOH)	difference, V[a]	ref
1,4-benzoquinone	0.711	0.000	8a
phenyl-1,4-benzoquinone	0.698	0.013	9b
methylbenzoquinone	0.656	0.055	8a
2,5-dimethylbenzoquinone	0.597	0.114	8a
1,4-naphthoquinone	0.493	0.218	8b

[a] Difference from 1,4-benzoquinone.

an excellent guide to the choice of compounds to be studied. Some of their results are given in Table II. These data show a great variation in the effect of substituents on the redox potential of benzoquinone. Thus, substitution of a phenyl group on the quinone ring has very little effect with a lowering of the potential of only 0.013 V. A methyl group has an appreciably greater effect, stabilizing the quionone with respect to the hydroquinone form by 0.055 V. The value for 2,5-dimethylquinone shows an approximately additive effect of the two methyls on the reduction potential. By far the largest effect is provided by the fusion of a second ring in naphthoquinone with a stabilization of the quinone relative to the hydroquinone of 0.218 V.

Approximate equilibrium constants for some solution equilibria of interest are presented below as calculated from the results in Table II.

$$\mathbf{3a} + \mathbf{4b} \rightleftharpoons \mathbf{3b} + \mathbf{4a} \quad K = 70 \tag{1}$$

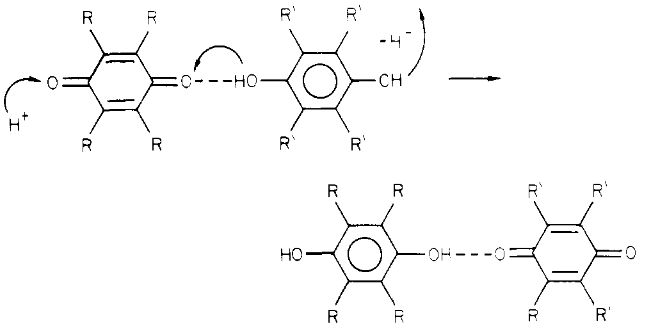
$$\mathbf{3a} + \mathbf{6} \rightleftharpoons \mathbf{5} + \mathbf{4a} \quad K = 7000 \tag{2}$$

$$\mathbf{3a} + \mathbf{8} \rightleftharpoons \mathbf{7} + \mathbf{4a} \quad K = 2 \times 10^7 \tag{3}$$

$$\mathbf{3c} + \mathbf{8} \rightleftharpoons \mathbf{7} + \mathbf{4c} \quad K = 9 \times 10^6 \tag{4}$$

All of these equilibria lie well to the right in solution. The large values (10^7) of the constants for the equilibria 3 and 4 leading to the complexes of naphthoquinone (**7**) with hydroquinone (**4a**) or phenylhydroquinone (**4c**) are particularly interesting. Although there seems to have been no extensive study of these reactions in solution it had been reported by Urban[10] that an attempt to prepare the unsymmetrical quinhydrone **3a**/**8** by crystallization from a solution containing the components had given only the isomeric quinhydrone **7**/**4a**.

The solid–solid reaction described in a previous paper[5a] provided a means of synthesis of the desired unstable complexes in spite of the difficulty (thus far prohibitive) of preparing them by crystallization from a solvent. When the crystalline 1:1 complexes of benzoquinone (**3a**)/naphthohydroquinone (**8**) or phenylbenzoquinone (**3c**)/naphthohydroquinone (**8**) prepared by the solid–solid reaction described previously[5a] were heated at 70–80 °C for 3 h, they were converted essentially quantitatively to the isomeric quinhydrones **7**/**4a** or **7**/**4c** as shown by the fact that the FTIR spectra and X-ray powder photographs of the products were identical with those of the corresponding complexes prepared by either a solid–solid reaction or by crystallization of the product quinhydrone from solution. The quinhydrone complex formed in each case is thus not only microcrystalline but also has the same crystal structure as the product quinhydrone obtained by crystallization from solution. It may be noted that the crystal structure of the product **7**/**4a** had been shown[11] to contain the quinone and hydroquinone components alternating to form hydrogen-bonded chains which are further held together by π complexing to form layers. The oxidation–reduction reaction involves in the simplest formulation removal of a hydrogen ion (or a hydride ion) from one end of a hydrogen-bonded quinhydrone chain accompanied by a series of hydrogen transfers converting each hydroquinone to a quinone and vice versa and finally re-addition of the hydrogen ion (or hydride ion) to the molecule at the other end of the chain.



Clearly, however, the mechanism (which has yet to be carefully studied in solution) is much more complicated and is accompanied by extensive reorganization of the structure.

The products formed in these two cases are those highly favored in the solution equilibria. It is reasonable that, as initially proposed, the energy of activation of the solid-state reaction is lowered by the greatly increased stability of the product quinhydrone relative to the starting complex and the rate of reaction thus increased. While it is impossible to express the extent of this increase in any quantitative way until more is known about the reaction kinetics, our observation of complete conversion in these reactions after 3 h at 80 °C can be compared with the reaction velocity of the exchange undergone by the unsymmetrically deuterated but otherwise unsubstituted quinhydrone (**1a**) studied by Brodskii and Gragerov who found about 10% conversion to **2a** at 107 °C in 3 h. The relative free energies of the isolated molecules of starting material and product, the molecular mobility, and other factors should play a major role in determining the rate.

The solid-state reactions have some interesting aspects not found in solution chemistry. Once the conversion of a complex such as **3a**/**8** has proceeded part way there are present in the reacting mixture two quinones (**3a** and **7**) and two hydroquinones (**4a** and **8**), which might be imagined to recombine to form the symmetrically substituted complexes **3a**/**4a** and **7**/**8**. Examination of the FTIR spectra of reaction mixtures at various stages of reaction showed that these symmetrically substituted complexes never build up to a detectable extent. They may, of course, be present in amounts too small to detect by the methods we have employed. Furthermore, the redox rearrangement of **3a**/**8** to **7**/**4a** seems to be thermodynamically controlled. Of all species that might be formed, the most stable is complex **7**/**4a**; thus, an equimolar mixture of the four solid components **3a**, **4a**, **7**, and **8** gave, after heating, only the complex **7**/**4a**.

Perhaps the most interesting reaction was the rearrangement of the 1:1 complex of the unsubstituted quinone **3a** with the dimethylhydroquinone **6**. The equilibrium for this reaction is in solution considerably less one-sided than those above, the K estimated from reduction potentials being only 10^4 rather than 10^7 as found for the reactions just discussed. Furthermore, in contrast to the 1:1 composition of the starting complex, the components **5** and **4a** to be expected from the redox reaction were found[5a] to form, either when brought together in a solid–solid reaction, or when gel diffusion is used, or when mixed in a solvent, a complex of quinone **5** and hydroquinone **4a** in a ratio of 1:2 rather than 1:1. When the 1:1 complex of **3a** and **6** was heated at 80 °C for 8 h, it did indeed undergo rearrangement with the production of a complex of the redox products. The complex so formed was, however, not the 1:1 complex as had been found with the previous rearrangements but the 1:2 complex of **5** and **4a**, identical with that prepared directly from the components; the extra molecule of quinone **5** separated to form independent microcrystals, which gave rise to the expected absorption bands in the FTIR of the mixture. Similar results were obtained when the 1:1 complex of quinone (**3a**) and methylhydroquinone (**4b**) was heated at 75 °C for 10 h except that when the mixture was heated the methylquinone, which formed along with the 1:2 complex of **3b** and **4a**, sublimed out of the reaction mixture and only the 1:2 complex

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(9) (a) Hunter, W. H.; Kvalnes, D. E. *J. Am. Chem. Soc.* **1932**, *54*, 2869–2881. (b) Kvalnes, D. E. *Ibid.* **1934**, *56*, 2478–2481.

(10) Urban, G. *Ber.* **1908**, 299–318.

(11) Thozet, A.; Gaultier, J. *Acta Cyrstallogr., Sect. B* **1977**, *B33*, 1052–1057.

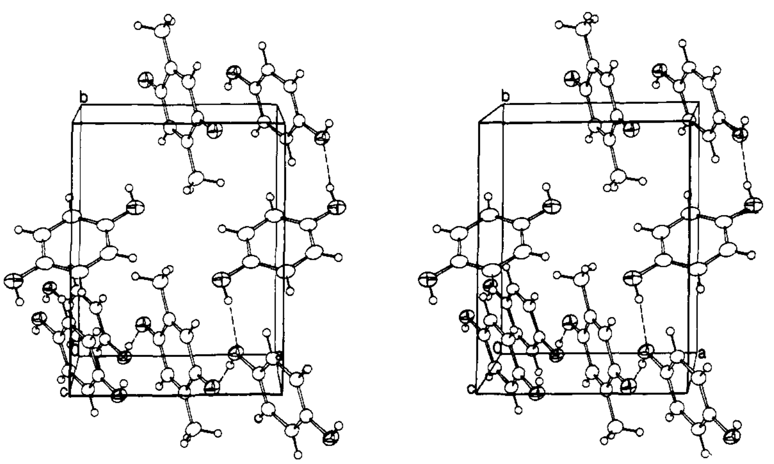

Figure 4. Stereoscopic view of the packing of the 1:2 complex, showing the unit cell. The reference for the first hydroquinone molecule is at the center (1,0,1), while that for the second hydroquinone molecule is at the center ($1,^1/_2,^1/_2$); the reference for the dimethylbenzoquinone molecule is at the center ($^1/_2,0,^1/_2$). Hydrogen bonds are shown be discontinuous lines. Some symmetry-related molecules are omitted in order to reduce overlap.

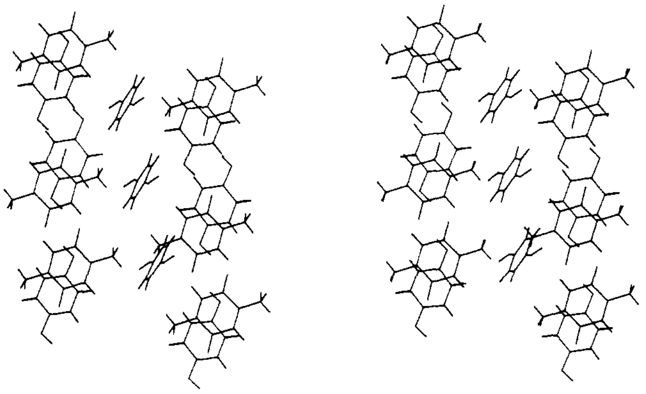

Figure 5. Complex of 2,5-dimethylquinone (**5**) with hydroquinone (**4a**) (1:2) viewed looking onto the ($\bar{2}01$) plane. The vertical direction in the plane of the page is [102]. The direction of translation to the left is the direction [011]. The lower layer is formed from the upper by translation along *c*. The [001] direction out of the plane of the page is defined by the three interstitial hydroquinone molecules shown hydrogen bonded to the quinhydrone strips.

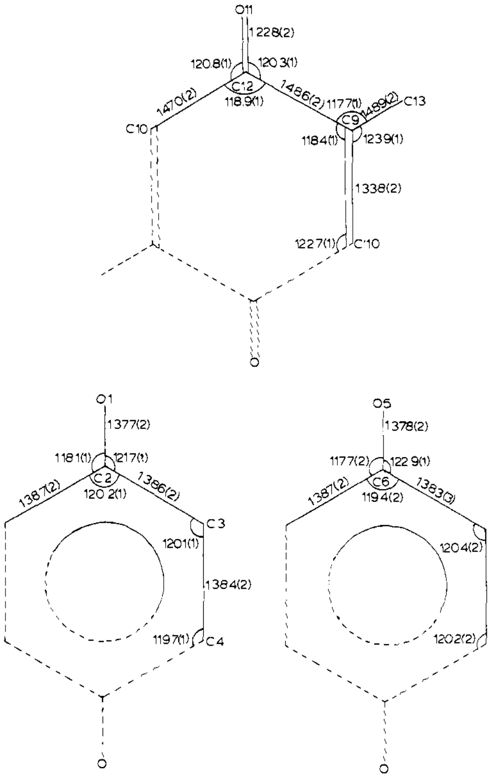

Figure 6. Bonds lengths (Å) and angles (deg) in the dimethylbenzoquinone (upper) and two hydroquinone (lower) "half-molecules".

could be identified in the FTIR spectrum. A further difference was that in this case the ratio of **3a** to **4b** varied somewhat (from 1:1.5 to 1:2). In this case the equilibrium in solution is still less one-sided (with K_{eq} approximately 10^2). Phase diagrams were constructed by determining the behavior on melting of mixtures of naphthoquinone with hydroquinone, dimethylbenzoquinone with hydroquinone, and methylbenzoquinone with hydroquinone. There was evidence of complex formation as anticipated: a maximum in the melting point diagram at a composition of 1:1 in the first case and approximately 1:2 in the other two.

A reinvestigation of the aryl-substituted complex **3d**/**4c** has shown that there was a slow reaction when the complex was heated. Thus, there were pronounced changes in the infrared spectrum when the complex was heated at 130 °C for 15 h. The complications introduced by the possible formation of four complexes of nearly equal energy (**3c**/**4d**, **3c**/**4c**, **3d**/**4d**, and **3d**/**4c**) has made study of this system less attractive and it has not been further investigated.

The nature of the 1:2 complexes is of considerable interest since complexes of quinones with hydroquinones have previously been found[1] to contain the components in a ratio of 1:1. The crystal structure, determined by X-ray diffraction, is shown in Figure 4. The basic structural unit is the hydrogen-bonded chain of alternating quinone and hydroquinone units as is found in almost all quinone/hydroquinone complexes (Figure 5). These chains are stacked together to form layers, the stacks being held together by π overlap; a quinone molecule lying over a hydroquinone and vice versa as is normal for quinhydrone structures.[1] The planes of overlapping quinone and hydroquinone rings are inclined at an angle of 7.14°; the C(12)=O(11) group of the quinone lies over the plane of the hydroquinone ring, with best plane–C(12) and –O(11) distances of 3.29 and 3.39 Å, respectively. The C(2)–O(1)H group of the hydroquinone ring lies over the plane of the quinone ring, with best plane–C(2) and –O(1) distances of 3.20 and 3.04 Å, respectively. The noteworthy difference between this complex and other quinhydrones is that the adjacent hydrogen-bonded strips, normally in edge-to-edge contact, are separated because of the steric effect of the methyl groups; the extra hydroquinone molecules are inserted vertically to form hydrogen-bonded cross-links between alternate hydroquinone strips. These hydrogen bonds involved in the cross-linking are between pairs of phenolic hydroxyl groups and seem to be responsible for the unusual IR absorption at 3380 cm^{-1} (Figure 3), unusual both because of its narrow width and high frequency compared to other solid state O–H stretching absorptions observed in the FTIR spectra of quinhydrones and phenols.

The crystal structure of the 1:2 complex of **5** and **4a** is in the space group $P\bar{1}$ with all three molecules (one quinone and two independent hydroquinones) sitting on centers of symmetry (Figure 4). Bond lengths and angles are shown in Figure 6. There is excellent agreement between the molecular dimensions of the two independent hydroquinone "half-molecules". An interesting feature of the geometry of the dimethylbenzoquinone molecule is the significantly greater length of the C(12)–C(9) $(-CH_3)$ bond as compared to the C(12)–C(10) (–H) bond and the smaller C(12)–C(9)–C(13) angle as compared to C(10′)–C(9)–C(13). Both hydroquinone rings are planar within the accuracy of the analysis, and the hydroxyl oxygen atoms lie 0.003 and 0.019 Å from the respective planes. The ring of the quinone molecule is also planar, with O(11) and C(13) lying 0.027 and −0.035 Å from the plane.

One set of independent hydroquinone molecules of the complex forms an infinite chain in the [101] direction with the quinone molecules by OH---O hydrogen bonding. The quinone and hydroquinone molecules forming this chain lie in the $(\bar{1}01)$ plane. The O(1)–H hydroxyl group acts as a donor to O(11) of the quinone molecule. The O(1)---O(11) distance is 2.732 (2) Å, the H(1)---O(11) distance is 1.77 (2) Å, and the O(1)–H(1)---O(11) angle is 172 (2)°. Sandwiched between chains separated by the *b*-axis parameter lie the other set of hydroquinone molecules. These molecules are inclined at almost right angles to the first set and are linked to them by O(5)–H---O(1)(–H) hydrogen bonds. The O(5)---O(1) distance is 2.775 (2) Å, the H(5)---O(1) distance is 1.95 (3) Å, and the O(5)–H(5)---O(1) angle is 167 (2)°. Inspection of the structure suggests that the nonstoichiometric amounts of benzene found upon crystallization from that solvent result from partial replacement of the cross-linking hydroquinone molecules by benzene molecules.

The structure of the 1:2 complex of 2,5-dimethylbenzoquinone **5** with hydroquinone **4a** thus differs in a most interesting way from that[5b] of the 2:1 complex of **5** with 2,5-dimethylhydroquinone (**6**). Each structure is layered with a basic unit of hydroquinones hydrogen bonded to quinone molecules. The unusual stoichiometries in the two structures have as a common origin the steric repulsion of the methyl groups of adjacent molecular strips. However, the extra molecule is incorporated in a quite different manner here than in the previous structure[5b] where the normal quinhydrone chains were reduced to triplets, each hydroquinone being hydrogen bonded to two quinone molecules but with the hydrogen-bonded chains not continuing beyond that point. It has not yet been possible to obtain single crystals of the unstable isomer **6/3a** suitable for structure determination but it is most interesting that the unstable isomers formed by both the 2-methyl- and 2,5-dimethyl-substituted hydroquinones with unsubstituted benzoquinone have, unlike the stable isomers, the more usual 1:1 stoichiometry.

Conclusions

In spite of the extensive structural change required for redox reactions of unsymmetrically substituted quinhydrones in the solid state, it has been found that such reactions may, in favorable cases, proceed essentially quantitatively under relatively mild conditions; the equilibrium lies in the direction predicted from earlier redox measurements in solution. In those cases where the 1:1 complex of the product quinone and hydroquinone is unstable with respect to the 1:2 complex, the latter is formed, and the product obtained appears to be a mechanical mixture of the 1:2 complex with the superfluous quinone which has separated into its own microcrystallites. The products of these reactions thus are controlled by the energetics of crystal packing rather than by the stoichiometry of the starting quinhydrone.

Acknowledgment. We are indebted to the National Science Foundation for support of this work. The computer program MULTAN 80 and RANTAN employed in the structure determination were written by members of Professor M. M. Woolfson's group at the University of York, England, and the refinements were carried out using SHELX (G. M. Sheldrick, Cambridge University, England).

Registry No. Benzoquinone/naphthohydroquinone 1:1 complex, 87970-33-0; phenylbenzoquinone/naphthohydroquinone 1:1 complex, 87970-35-2; benzoquinone/2,5-dimethylhydroquinone 1:1 complex, 87970-32-9; benzoquinone/2-methylhydroquinone 1:1 complex, 55836-33-4; naphthoquinone/hydroquinone 1:1 complex, 60706-28-7; naphthoquinone/phenylhydroquinone 1:1 complex, 87970-34-1; 2,5-dimethylbenzoquinone/hydroquinone 1:2 complex, 87970-37-4; 2-methylbenzoquinone/hydroquinone 1:2 complex, 87970-36-3.

Supplementary Material Available: Tables of thermal parameters, details of plane calculations, and observed and calculated structure factors for the 1:2 complex (12 pages). Ordering information is given on any current masthead.

Comparative Photophysics of Platinum(II) and Platinum(IV) Porphyrins

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Abstract: Absorption changes and kinetic behavior produced by excitation of $Pt^{II}(TPP)$ and $Pt^{IV}(TTP)Cl_2$ with 35-ps flashes at 355 and 532 nm are reported. (TPP is tetraphenylporphyrin; TTP is tetratolylporphyrin.) The transient difference spectrum obtained for the Pt(II) compound persists for >10 ns and is assigned to the lowest ring triplet, $^3T(\pi,\pi^*)$. Similar results were found for $Pd^{II}(TPP)$. On the other hand, the absorption changes obtained for the Pt^{IV} compound decay rapidly, with a time constant of 45 ± 10 ps. This transient behavior is ascribed to a low-lying ring-to-metal $[a_{2u}(\pi),d_{x^2-y^2}]$ charge-transfer state predicted by theory.

Extensive experimental and theoretical investigations of the electronic structure of metalloporphyrins, their excited states, and interconversion processes have been carried out over the past 3 decades.[1] Much of the experimental work has focused on the ground-state absorption, fluorescence emission from the lowest excited singlet, $^1Q(\pi,\pi^*)$, and phosphorescence emission from the lowest excited triplet, $^3T(\pi,\pi^*)$. However, there are a rather large number of transition-metal porphyrins that can be characterized

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