STRUCTURE AND OXIDATION-REDUCTION CONVERSIONS OF QUINHYDRONE COMPLEXES

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UDC 541.6:542.941:542.943:541.49:547.567

One of the important examples of donor-acceptor complexes with an H bond is the so-called quinhydrones, which are complexes of quinones and hydroquinones that are formed by a π bond and a system of H bonds. By virtue of the various steric requirements imposed by the π bond and the H bond, the coexistence of these two types of interactions in the ordered quinhydrone structure depends to a large extent on the structures of the interacting molecules. The simplest representative of this series of complexes, which is formed by p-benzoquinone and hydroquinone, is a conventional donor-acceptor complex in solution [1]; in the crystal, besides the π bond (3.16 Å interplanar distance), there appears a moderately strong 0...HO H-bond (2.72 Å) [2]. Systematic investigations of the spectral and thermochemical properties of quinhydrones were begun in [3, 4]. It was shown that the charge transfer energy depends on the state of the H bond, and consequently on the structure of the crystalline complex. It was also found that the activation energy of the redox reactions of the complexes is close to the energy of charge transfer (CT).

The low-lying excitation states of donor-acceptor complexes with a H bond are responsible for the thermal transfer of an electron and a H atom [5]. Therefore the study of these states, using quinhydrone complexes as an example, becomes important in the elucidation of chemical reaction mechanisms, in particular polymerization. The present work studies the spectral properties and the reactions of a number of p-benzoquinone and hydroquinone derivatives. It discusses the steric and electronic effects of substituents on complex structure, CT energy, and reaction kinetics.

EXPERIMENTAL

UV spectra were obtained with a Specord UV-VIS spectrophotometer with thermostating accessories. Complex samples were studied compressed with KBr, in mineral oil, and in solution. IR spectra were obtained with a UR-20 spectrophotometer in the 400-4000-cm⁻¹ region. Samples were prepared by mixing in a mortar for 1-2 min and compression with KBr. With more prolonged mixing, mechanochemical reactions occur. For kinetic measurements samples in KBr disks were placed in a thermostated block. The time for temperature establishment did not exceed 40 sec. Cl-, Br-, and Me-substituted p-benzoquinones (CBQ, BrBQ, MBQ) and the respective hydroquinones (CHQ, BrHQ, MHQ) were synthesized from ortho-substituted phenols, and by chlorination or bromination of BQ. The reagents were purified by crystallization and sublimation.

DISCUSSION OF RESULTS

The donor-acceptor complex of p-benzoquinone (BQ) and hydroquinone (HQ) forms by the overlap of the upper occupied molecular orbital (UOMO) of HQ with the lower free orbital (LFMO) of BQ. Electron transfer between the ground and excited states is recorded as a CT band in the absorption spectra of the complex (Fig. 1). The location of the CT bands is determined by the well-known relationship:

$$E_{\rm CT}^{\ \pi} = I_{\rm D} - E_{\rm A} + W \tag{1}$$

Since in the quinhydrone complexes that were studied (Table 1), the CT bands in solution obey Eq. (1), the conventional π complexes exist in solution without a noticeable H-bond contribution. It must be said that in the dual BQ/HQ complex with plane-parallel alignment of the BQ and HQ molecules at 3.2-3.3 Å distance, only a nonlinear 0...HO H-bond can form, with 0...HO angle about 120°; as is known, its energy is low. It can be assumed that the quinhydrone structure (A...H...D) is not stable in the dual complex.

Institute of High Molecular Weight Compounds, Academy of Sciences of the USSR, Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 95-103, January 1985. Original article submitted July 1, 1983.

Comp	hex		hv _{CT} , cm ⁻¹				
		solic	l phase	·	-	-	Preexponential
>=0	HO	in KBr	in mineral oil	solution	vон, ст. ¹	Ea. CIT-	term
R ¹	R ²						
Н	Н	17500	16000	24000 AN*	∕ 3230, 3300 sh†	17400 [6]	31 [6]
C	Н	16600	15500	19800 THF	3255	14600 [3]	22,9
Н	ច	17800	17000	26000 CHCl ₃	3270		
Н	Me	16800	16200	22800 CHCI3	3260, 3320 sh	14300	24
Me	Н	18000	18000	25000 AN	3240, 3390		
Br	Н	16400	15200	19800 THF	- 3250	12900	20
Н	Br	17700	17000		3230		
ច	Me	16000	14500 - 15400	21000 CHCl ₃	3300	12200	21
Me	ð	18500	18500	Z7000 CHCl,	3230		
Br	Me	16000	14500-15000	19500 THF	3280	12200	21
Me	Br	18500		27000 CHCIs	3230		
*MeCN. †Shoulder.							

TABLE 1. Spectral and Thermochemical Properties of Complexes

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Fig. 1. UV spectra of BQ/HQ complexes (1-3)and the BQ polymerization product (4): 1) solution in MeCN, 20°; 2) compressed with KBr; 3) solution in MeCN-CHCl₃ mixture (1.5:1) at -40° after precooling to -60°; 4) solution in water.



(2)

and that equilibria a and b are predominant, with participation of the (A...DN) π -complex and the (A...H-D) H-bond.

 $\begin{array}{c}
a \\
A + HD \rightleftharpoons (A \cdots H \cdots D)^{*} \rightleftharpoons (AH', \dot{D}) \\
\downarrow & \downarrow & \downarrow \\
(A \cdots DH) \quad (A \cdots H - D) \quad (A \cdots H \cdots D)
\end{array}$ (3)

In solution the (A...H...D) structure is established apparently with participation of solvent molecules or by association of several BQ and HQ molecules, but the existence of structure (2) as collision complexes cannot be excluded. In contrast to the solution, effective UOMO and LFMO overlap occurs in the crystal in the presence of the H-bond network.

The H-bond effect in such a complex consists of the stabilization of the excited level of the complex by conjugation of the π donor systems of and acceptor. The stabilization energy E_{stab} is of the order of magnitude of a H-bond in the excited state and is a function of the steric structure and acid-base properties of the interacting molecules. The transition energy of (A...H...D) \rightarrow (A...H...D)* decreases by E_{stab} from Eq. (1):

$$E_{\rm CT}^{\rm H} = E_{\rm CT} - E_{\rm stab} \tag{4}$$

Such transitions can be observed experimentally in absorption spectra or pulsed spectra of the $S_1 \rightarrow S_2$ type. By virtue of the high rate of nonradiating transitions, the observation of transmission spectra is very much more likely. An important feature of the (A...H...D)* excited states is their participation in transfer of an electron, H⁺, and a H atom. The sequence of these processes depends on the donor-acceptor and acid-base properties of the remagent molecules and the nature of the solvent.

SPECTRAL PROPERTIES OF COMPLEXES

<u>BQ/HQ</u>. In solution the complex is characterized by a broad CT band with maximum at 24,000 cm⁻¹ (see Fig. 1). Since the electron affinity of BQ is 1.8 eV, while $I_d(HQ) = 7.8$ eV, then when W = -3.2 eV, $E_{CT} = 22,400$ cm⁻¹. Consequently the complex appears to have predominantly π - π * character. The significant low-frequency shift when the complex is crys-

tallized, reaching 8000 cm⁻¹, is due to the effect of the H bond in the excited state. It is noteworthy that compression with KBr causes a noticeable high-frequency shift for practically all the complexes, as compared with trituration in mineral oil. This can be related to some disruption of packing in the crystal during compression. The IR spectra of the crystalline BQ/HQ complex shows a high-frequency shift of the C=O deformation vibrations from 416 to 448 cm⁻¹, and a low-frequency shift of the C=O valence vibration band 1655 \Rightarrow 1633 cm⁻¹, indicating the formation of a O...HO H-bond.

Since the CT band is extremely sensitive to the structure of the complex, by varying the conditions of complex synthesis and the properties of the medium we can try to approach the low-frequency limit of hv_{CT} . In a CHCl₃-MeCN mixed solvent a blue BQ/HQ complex could be obtained (see Fig. 1) that is stable in the -40 to -60° range, and is converted reversibly to a conventional π complex. Under these conditions microcrystals of complex form that apparently include solvent molecules. The 13,500 cm⁻¹ CT band is shifted by 10,500 cm⁻¹ relative to the solution band; this is convincing evidence for the significant role of the H bond in quinhydrone formation. Figure 1 also shows the absorption spectrum of the BQ polymerization product, which according to the IR spectrum contains quinoid and hydroquinoid monomer units. The polymer spectrum is not very sensitive to temperature or kind and concentration of solvent; we can therefore speak of an intrachain reaction of those units. Evidently in this case a continuous spectrum of states is obtained which causes continuous absorption in the visible, due to the black color of these compounds.

<u>BQ/MHQ, MBQ, HQ.</u> The BQ/MHQ complex is distinguished from the MBQ/HQ complex with which it is conjugated by the fact that in the former case the Me group intensifies the electrondonor properties of HQ, whereas in the latter case it weakens the acceptor properties of BQ. This is attributed to the high-frequency shift of the CT band in solution, which amounts to 2200 cm⁻¹ in going from BQ/MHQ to MBQ/HQ. In the crystalline state both compounds have the quinhydrone structure; this is evidenced by the substantial decrease of CT energy, as the $E_{CT}^{CT} = C_{CT}^{CT}$ difference assumes the largest value for the weaker complex. The IR spectra also show signs that point unequivocally to the formation of an quinhydrone structure: a noticeable high frequency shift of the $\delta C=0$ band, and the decreased frequency of the C=0 valence vibra-. tions and of one of the intense skeletal vibrations in the 900-1000-cm⁻¹ region. As Fig. 2 shows, the CO band splits into two components, that correspond to the two crystalline modifications of the complex, viz., "dense" at 450 cm⁻¹ and "porous" at 443 cm⁻¹. The MHQ vibrational bands undergo a similar splitting, "dense" at 723 cm⁻¹ and "porous" at 728 cm⁻¹. The proportions of these structures depends on the method by which the complex is prepared, but attempts to separate either form in a pure state were unsuccessful.

The conjugated MBQ/HQ complex is also represented by two structures. The 890-cm⁻¹ band corresponds to the energetically less favored "dense" structure; when heated at 50° the latter is quickly converted to the other modification ("loose") that is characterized by the 899-cm⁻¹ band. Noteworthy is the complicated absorption in the OH valence vibration region for the "loose" structure (see Fig. 2, spectrum 2). Analogous spectra, although not so clearly defined, are found for the other complexes. It can be presumed that the high-frequency 3390cm⁻¹ band belongs to the less weighted HQ hydroxyl, while the intense low-frequency 3240cm⁻¹ band is due to the stronger 0...HO H-bond. The presence of two kinds of H-bonds is apparently related to the difference in proton-acceptor properties of the two MBQ carbonyls.

We must mention the substituent steric factor, which can affect the structure of the complexes. It is known that methyl groups is substituted benzenes do not obstruct the formation of π complexes. But when a quinhydrone complex forms, the substituent volume becomes extremely important. Thus BQ and CBQ form π complexes with p-phenylenediamine that contain H bonds [4], whereas with MBQ such a complex cannot be obtained.

<u>BrBQ/HQ</u>, BQ, BrHQ. The properties of the BrBQ/HQ complex and its conjugated BQ/BrHQ complex are close to those of the respective chlorosubstituted BQ and HQ [3]. In the crystalline state each complex is represented by two structures. One, which predominates when 10-15% excess HQ is present, can be called the "dense" structure of BrBQ/HQ; it is characterized by bands at 461, 887, and 980 cm⁻¹ that are related to BrBQ vibrations. The bands at 454, 891, and 974 cm⁻¹ belong to the "loose" BrBQ/HQ structure. In going from "dense" to "loose" the OH frequency increases in the region of OH valence vibrations.

CBQ/MHQ, MBQ/CHQ. In the CBQ/MHQ complex the substituents intensify the acceptor and donor properties of BQ and HQ, while in the conjugated MBQ/CHQ complex the substituent effect is the opposite. This accounts for the substantial difference in CT energy for the



Fig. 2. IR spectra of the BQ/MHQ complex immediately after mixing and compression with KBr (1); after 40 min heating at 52° (2); spectrum (3) was obtained when BQ and MHQ were mixed in the presence of CHCl₃, the solvent was quickly evaporated, and the residue compressed with KBr.

two complexes in solution, amounting to about 6000 cm⁻¹. The quinhydrone structure in the crystal is confirmed by spectral studies; the shift of CT band for MBQ/CHQ in going from solution to crystal reaches a maximum of 8500 cm⁻¹ (Fig. 3). In contrast to the complexes previously discussed, here the crystal contains only one modification. As can be concluded from the OH frequencies (see Table 1), in the conjugated MBQ/CHQ complex the O...HO H-bond is stronger than in CBQ/MHQ. Specifically because of the H bond there is a convergence of the E_{CT} values of these two complexes that are so different in donor-acceptor properties.

<u>BrBQ/MHQ</u>, MBQ/BrHQ. In spectral characteristics these complexes are close to the respective CBQ and CHQ complexes. It follows that the steric and electronic effects of Cl and Br as substituents in the donor and acceptor molecules in quinhydrone formation are identical. Some distinguishing features appear in the IR spectra. Thus the doublet of the MBQ C=O deformation vibrations at 405/442 cm⁻¹ shifts to 418/452 cm⁻¹ in MBQ/CBQ, and to 400/455 cm⁻¹ in MBQ/BrHQ.

REDOX REACTIONS OF COMPLEXES

In the solid phase and in solution, quinhydrone complexes undergo conversions in the direction of increasing the I_D-E_A difference. If the conjugated complex is identical with the starting complex, e.g., BQ/HQ and HQ/BQ, then the reaction is reduced to an interconversion of complexes. In the reaction



there is a transfer of two electrons and protons (overall from two H atoms) from a donor molecule to an acceptor. A similar reaction, according to [5] and Eq. (3), occurs through the electron-excited state of the complex, which has the features of a radical. In the present work we have studied only the reactions of crystalline complexes for which the excita







Fig. 4. Kinetic curves for change of optical density of $899-cm^{-1}$ band belonging to "loose" structure of MBQ/HQ, when BQ/MHQ is heated; 1) 42.5; 2) 48; 3) 56°.

tion energy of the (A...H...D)* state can be determined directly. The activation energy ${\rm E}_{\alpha}$ of the thermal reaction

$$k = k_0 \cdot \exp\left(-E_a/kT\right) \tag{6}$$

must be close to the CT energy. In the case of an ideal complex structure the conversion

 $A \rightarrow B$

can properly be considered as first order and described by the equation:

$$-\ln (1 - x/x_0) = k_1 t \tag{7}$$

where $k_{-1} = 0$. In an actual crystal there is a variety of states, which complicated the reaction kinetics.

An important feature of these systems is the strict equimolarity of the conversion of A to B while the crystal structure of the complex is retained practically without change. Therefore the kinetic curves can be constructed with respect to the concentration change of any of the four components of the system.

<u>BQ/MHQ</u>. Kinetic curves were constructed for the $899-cm^{-1}$ band that corresponds to the "loose" structure of the MBQ/HQ reaction product (Fig. 4) and for the $873-cm^{-1}$ band of the starting complex. The kinetic features obtained with these two methods of calculation are completely identical (Fig. 5). The time dependence of $-ln(1 - x/x_0)$ contains two distinct portions. The initial linear portion apparently corresponds to the reaction of the "dense structure" with 41 kcal/mole activation energy (14,300 cm⁻¹) and preexponential term 10^{A} =



Fig. 5. For determination of activation energy of reactions of BQ/MHQ (1) and CBQ/MHQ (2); points for (1) taken for 873- and 899-cm⁻¹ bands; points for (2) taken for 418-, 722-, and 1002^{-1} bands, with various methods of preparation of complexes,

 10^{24} sec⁻¹; such a large value for the latter is evidence for the cooperative nature of the reaction. The activation energy of the thermal reaction, 41 kcal/mole, is close to the CT energy in the crystal, 48 kcal/mole.

CBQ/MHQ. Kinetic curves were constructed for the bands at 722 and 1002-cm⁻¹ which belong to the MHQ and CBQ vibrations for the starting CBQ/MHQ complex, and for the 418-cm⁻¹ band that is related to the reaction product MBQ/CBQ. The kinetic relations $-\ln(1 - x/x_o)/t$ are linear, which indicates that a single process is taking place. This agrees with the data on the presence of a single crystal modification of CBQ/MHQ. It is important to note that different methods of measurement give identical values for the rate constants (see Fig. 5). The activation energy is 35 kcal/mole when A = 21. Comparison of the CBQ/HQ and CBQ/MHQ complexes of similar structure shows a distinct relation between the change in ECT and E_{α} .

BrBQ/MHQ. The kinetic curves for the decrease in concentration of the starting complex were constructed for the MHQ and BrBQ bands at 722 and 975-cm⁻¹ respectively. In all details the kinetic features of this reaction are similar to those of the CBQ/MHQ reaction; the activation energies, 35 kcal/mole, and the preexponential term, A = 21, also coincide.

The E_{α} values shown in Table 1 are reproducible within 10% for this series of compounds, so that we can speak with confidence of a correlation between E_{α} and E_{CT} . At the same time there are systematic errors due to insufficient chemical purity and structural homogeneity of these complexes. In particular, acid catalysis of the reaction is possible due to traces of impurities. The origin of the initial rapid section of the kinetic curves is not completely clear. In the course of subsequent investigations the roles of the chemical and structural factors in the course of the reaction will be more exactly defined.

CONCLUSIONS

1. Chloro-, bromo-, and methyl-substituted p-benzoquinones and hydroquinones in the crystalline phase form quinhydrone complexes that contain a π bond and a network of 0...HO hydrogen bonds. The hydrogen bond causes significant stabilization of the excited level of the complex that reaches $10,500 \text{ cm}^{-1}$.

2. In the crystalline phase the activation energy of the redox reactions of the complexes is close to the energy of the CT complexes.

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