

Fourier Transform Infrared Studies of Halogenated Quinone Charge-transfer Complexes

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Introduction

Quinone molecules contain a highly conjugated π system which includes both the ring carbon-carbon bonds and the carbon-oxygen double bonds (carbonyl groups). The antibonding orbitals of this delocalized π system give the quinone structure the capacity to function as a Lewis Acid and accept electron density from donor molecules. This transfer of electron density from the donor molecule to the quinone acceptor forms a charge-transfer bond between the two molecules and results in the formation of a charge-transfer complex (1). The increase of the electron density in the quinone antibonding orbitals causes the bond order of the carbon-oxygen double bonds on the quinone molecule to decrease and results in the decrease in the infrared vibrational frequency of the carbonyl bonds. The magnitude of the decrease in both the bond order and the vibrational frequency of the carbonyl bond is dependent on the extent of electron density transferred, the strength of the acceptor, and the strength of the donor, and it reflects the stability of the charge-transfer complex.

The quinone structure is a basic unit of a number of biologically interesting compounds, vitamin K, plastoquinone, and coenzyme Q. The study of the charge-transfer complexes formed between the quinone structure and donor molecules is important to the understanding of the kind of bonding that takes place in a number biologically interesting processes (1, 4, 2, 7, 8, 9). In this study the charge-transfer complexes of tetrahalo-1,4-benzoquinones (*p*-fluoranil, *p*-chloranil, and *p*-bromanil) and a series of donor molecules (polyalkylated aromatic and a special amine super donor, tetrakis(dimethylamino)ethylene) were prepared, and Fourier transform infrared spectroscopy was used to determine the position of the quinone carbonyl vibrational absorption in the complexes. A sandwich structure of the aromatic-quinone charge-transfer complex is pictured in Figure 1. The magnitudes of the shifts to lower wavenumbers of the

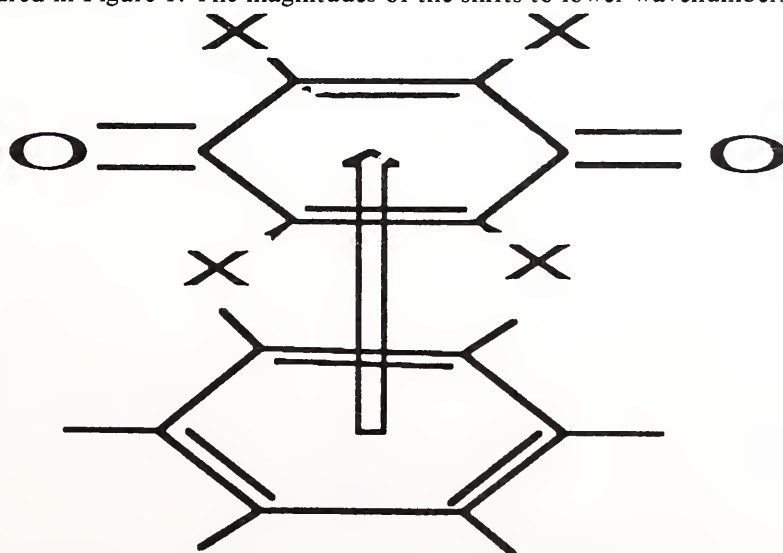


FIGURE 1. A Tetrahalo-1,4-benzoquinone-aromatic Charge-Transfer Complex.

carbonyl stretching absorptions in the complexes relative to the same stretching absorption in uncomplexed quinones were determined and related to the strength of the donor, the strength of the acceptor, and the stability of the complex.

Experimental

Each of the quinone-aromatic complexes was prepared by dissolving equimolar amounts of the quinone and aromatic compound in dichloromethane and allowing the resulting solution to evaporate. Tetrakis(dimethylamino)ethylene is an oxygen sensitive compound, and therefore its quinone complexes were prepared in an inert atmosphere glove box following the method described in the literature by H. E. Winberg (10). Although tetrakis(dimethylamino)ethylene is air sensitive, its complexes with the halogenated quinones were stable enough in the atmosphere so that no special methods were needed to record their infrared spectrum.

The infrared spectra of the complexes were recorded on a Digilab FTS 40 Fourier Transform Infrared Spectrometer. The spectra of the complexes were collected at 2 cm^{-1} resolution in a KBr matrix. The complex concentrations in KBr were adjusted to be 2% by mass for each complex. Multiple sample preparations were carried out for each complex and the spectra recorded for each of these samples to determine the dependence of the position of the carbonyl absorption on the complex concentration in the KBr matrix. For the experimental variations in concentration of the complexes due to sample preparation, no more than a 0.2 cm^{-1} shift in the carbonyl absorptions was observed due to matrix effects.

Results and Discussion

Fourier transform infrared spectroscopy with its high sensitivity and its ability to determine accurately the positions of vibrational absorption bands is well suited for this type of study of the stability of the charge-transfer complexes. The vibrational absorptions of the quinone carbonyl bonds in these charge-transfer complexes are located in a region from 1700 to 1650 cm^{-1} . Figures 2-4 show the spectra of the carbonyl bonds

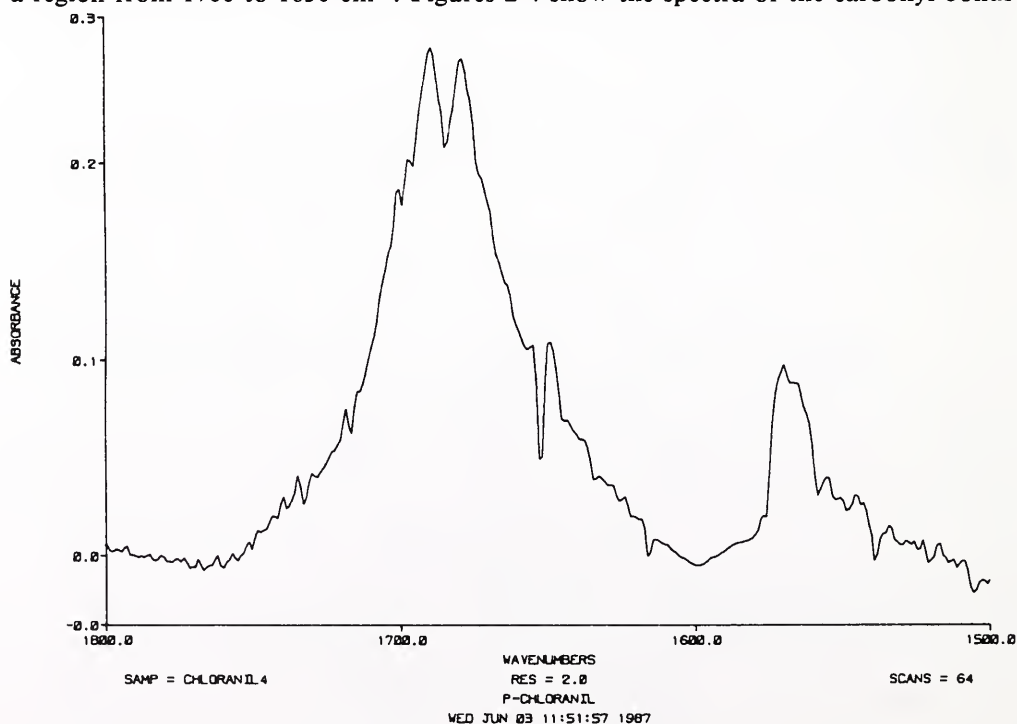


FIGURE 2. Spectra of Chloranil.

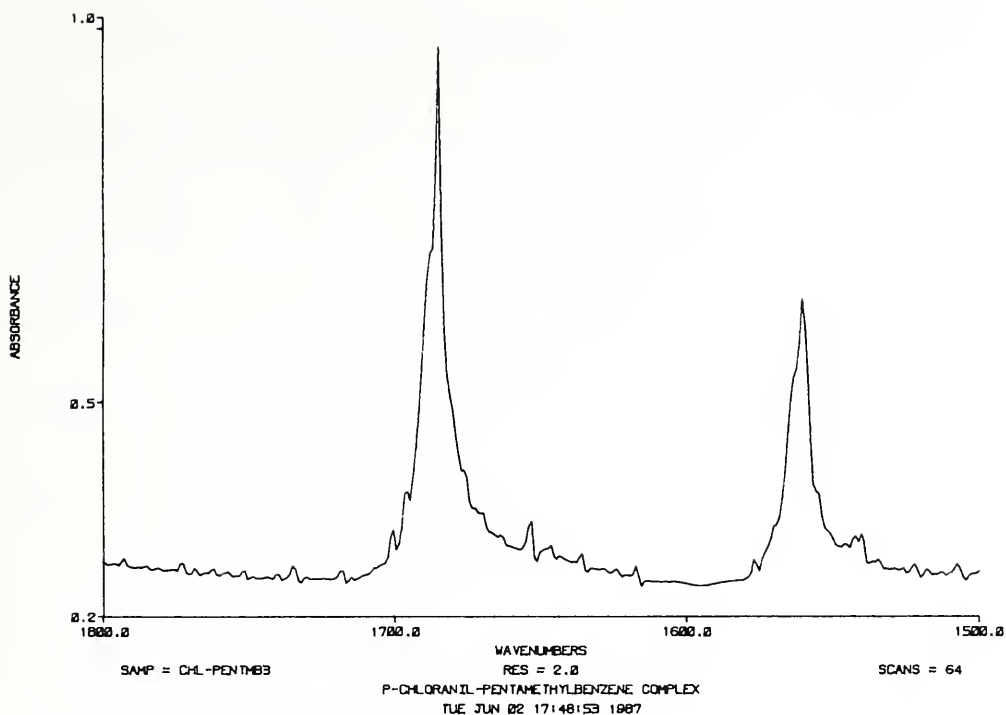


FIGURE 3. Spectra of Chloranil-Pentamethylbenzene Complex.

for chloranil and some selected complexes. The positions of the carbonyl vibrational absorptions and the shifts of these absorptions relative to the uncomplexed quinones are listed in Table I. The vibrational absorption positions are functions of the bond orders of the carbonyl bonds. The donation of electron density into the antibonding orbitals

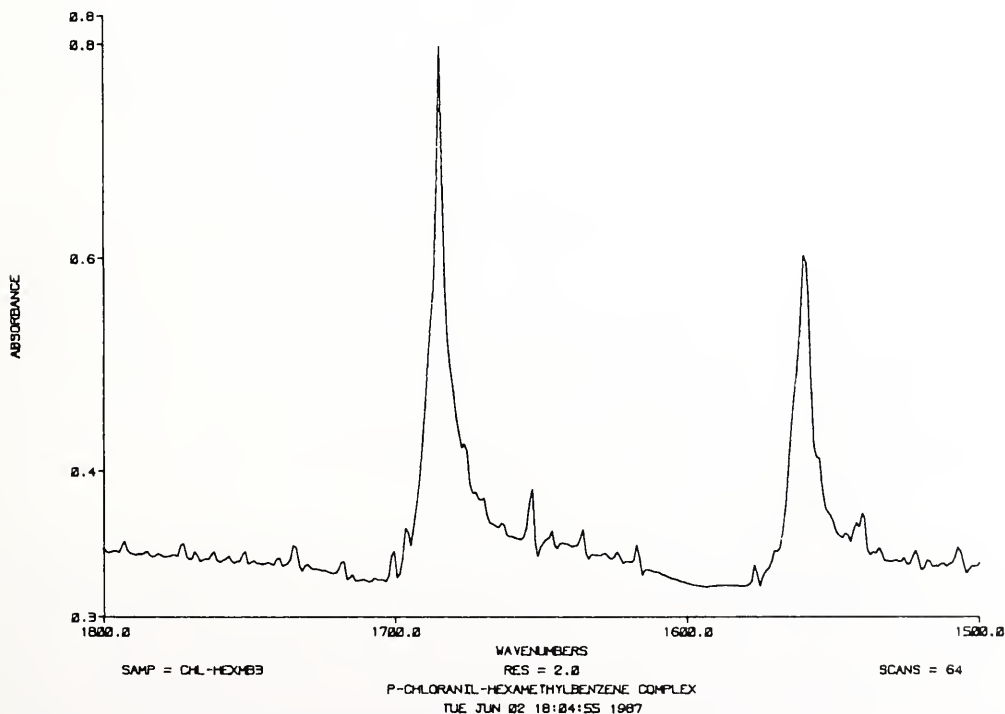


FIGURE 4. Spectra of Chloranil-Hexamethylbenzene Complex.

TABLE I. CO vibrational absorptions and absorptions shifts for tetrahalo-1,4-benzoquinone charge-transfer complexes.

Complex(donor-acceptor)	$\nu_{\text{CO}}(\text{CM}^{-1})$	$\Delta_{\text{CO}}(\text{CM}^{-1})$
1,2,4,5-tetramethylbenzene-p-fluoranil	1695.5	4.9 ^a
	1679.0	
pentamethylbenzene-p-fluoranil	1694.6	5.8 ^a
hexamethylbenzene-p-fluoranil	1692.3	8.1 ^a
tetrakis(dimethylamino) ethylene-p-fluoranil	1675.1	25.3 ^a
1,2,4,5-tetramethylbenzene-p-chloranil	1689.6	0.0 ^b
	1679.0	
pentamethylbenzene-p-chloranil	1684.9	4.7 ^b
hexamethylbenzene-p-chloranil	1684.8	4.8 ^b
tetrakis(dimethylamino) ethylene-p-chloranil	1627.3	17.3 ^b
	1657.8	21.2
1,2,4,5-tetramethylbenzene-p-bromanil	1679.4	0.6 ^c
pentamethylbenzene-p-bromanil	1678.5	1.5 ^c
hexamethylbenzene-p-bromanil	1675.2	4.8 ^c
tetrakis(dimethylamino) ethylene-p-bromanil	1669.6	10.4 ^c

^a The shifts are relative to the fluoranil CO vibrational absorption at 1700.4 cm⁻¹.

^b The shifts are relative to the chloranil CO vibrational absorption at 1689.6 cm⁻¹.

^c The shifts are relative to the bromanil CO vibrational absorption at 1680.0 cm⁻¹.

of quinone acceptors by the aromatic donors and the tetrakis(dimethylamino)ethylene during complexation reduces the bond order of the carbonyl bonds and causes their vibrational absorptions to shift to lower wavenumbers. The magnitudes of these shifts are related to the extent of electron donation into the antibonding orbitals of the quinone acceptors which in turn is related to the strengths of the donor molecules, the acceptor strengths of the quinones, and the stability of the charge-transfer complexes. In this study the following three issues were addressed: acceptor ability of the quinones and its dependence on the electronegativity of the halogen, donor strength of the aromatic and its relationship to the extent of ring alkylation, and the relative donor strengths of the π aromatic donors and a σ amine donor.

Three tetrahalo-1,4-benzoquinone acceptors were used in this study, *p*-bromanil, *p*-chloranil, and *p*-fluoranil. For this series of acceptors the electronegativity of the halogen increases (Br-2.9, Cl-3.5 and F-4.0) causing more charge to be removed from the quinone ring and the acceptor strength of the quinone to increase. This increase in acceptor ability of the quinone allows more electron density to be accepted into its antibonding orbitals, and it results in a greater reduction in the carbonyl bond order and a greater shift to lower wavenumbers of the carbonyl infrared absorption. Examination of the spectral data in Table I shows that as a group the carbonyl shifts decrease going from *p*-fluoranil complexes (4.9, 5.8, 8.1, 25.3 cm⁻¹) to chloranil complexes(0, 4.7, 4.8, 17.3 cm⁻¹) to *p*-bromanil complexes (0.6, 1.5, 4.8, 10.4 cm⁻¹).

The aromatic donors used in this study were 1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene. In the complexes with these donors, the aromatic compound donates electron density from its π system to the quinone π antibonding orbitals. As the number of electron releasing methyl groups on the aromatic ring increases, the donor strength of the aromatic compound also increases (3, 5). The spectral data in Table I shows that the carbonyl shifts are largest for hexamethylbenzene and that they decrease as the number of methyl groups and the donor of the aromatic decrease.

Tetrakis(dimethylamino)ethylene is described in the literature as an extremely strong Lewis Base, a super donor (1). The large donor capacity of the tetrakis(dimethylamino)ethylene is the result of the lone pair electrons on the highly alkylated amine groups. Our studies show (Table I) that sizeable carbonyl shifts (25.3, 17.3, 10.4 cm^{-1}) to lower wavenumbers exist in the complexes of the tetrakis(dimethylamino)ethylene with fluoranil, chloranil, and bromanil. This is in complete agreement with a large donation of electron density from the lone pair electrons on the tetrakis(dimethylamino)ethylene into the quinone π antibonding orbitals, a significant reduction of the quinone carbonyl bond order, and a large shift to lower wavenumbers of the quinone carbonyl infrared absorption.

Acknowledgments

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