

Electron-transfer interactions of chloranil/bromanil with hexacyanometalate (4-), $K_4[M(CN)_6]$, where M = Fe, Ru and Os

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UV-visible spectrophotometric studies on the interactions of chloranil/bromanil with the hexacyanometalate(4-), $[M(CN)_6]^{4-}$ ions, where M = Fe, Ru and Os, in 20-70% (vol./vol.) aqueous dimethyl sulphoxide media at 27°C demonstrate the formation of the negative semiquinone ion (I) derived from the halonil. New absorption spectral bands are immediately formed after mixing. The positions of the new bands are neither affected by the medium polarity nor by the nature of the metal in the hexacyanometalate (4-) ions. The reaction equilibrium constants and the molar absorptivities of (I) have been calculated. Experimental results indicate that (i) chloranil is the more powerful electron acceptor halonil, (ii) the abilities of the $[M(CN)_6]^{4-}$ ions to interact with the halonils depend on their redox potentials and follow the order $Fe(II) > Os(II) > Ru(II)$, and (iii) the reaction equilibrium constants increase greatly with the increasing water content of the medium.

As a part of our research programme on the study of charge-transfer interactions¹⁻⁶ and in continuation of our earlier work⁴ on the charge-transfer interactions of chloranil with nicotine, we report here the results of our investigations on the interaction of chloranil/bromanil with the hexacyanometalates (4-), $K_4[M(CN)_6]$, where M = Fe, Ru and Os in 20-70% (vol./vol.) aqueous dimethyl sulphoxide. The aim of the present study is to investigate the effect of the variation of (i) the halo atoms of the halonil molecules, (ii) the redox potentials of the hexacyanometalate(4-) ions, and (iii) the medium composition, on the reaction process. Chloranil, as a well known organic acceptor^{7a}, was chosen as a model for the quinones encountered in biological systems⁸⁻¹². Electron-transfer interactions between chloranil/bromanil and the above mentioned hexacyanometalate(4-) ions have not been reported earlier.

Materials and Methods

Chloranil (Aldrich) was recrystallized repeatedly from benzene to get yellow platelets; m.p. 289°C. Bromanil was prepared by the method described earlier¹³ and was recrystallized from glacial acetic acid to get golden yellow flakes, m.p. 299°C. Potassium hexacyanoferrate(II) (Aldrich reagent) and potassium hexacyanoruthenate(II) (Heraeus) were obtained as commercial samples and used as such. Potassium hexacyanoosmate(II) was prepared according to published procedure¹⁴. Spectrophotom-

etric grade dimethyl sulphoxide (Aldrich) was used as such. Doubly distilled conductivity water was used in the preparation of water-DMSO mixed solvents.

Calculated amounts of chloranil or bromanil (1.5×10^{-3} mol dm⁻³) in dimethyl sulphoxide and the hexacyanometalate(4-) ion (1.0×10^{-3} mol dm⁻³) in water were transferred to a 10 ml dark coloured flask and the volume was made up to the mark by adding the desired amount of water and dimethyl sulphoxide. The initial concentration of chloranil/bromanil was varied in the range of $(0.10-10.91) \times 10^{-5}$ mol dm⁻³ while that of the hexacyanometalate(4-) ion was varied in the range $(0.98-11.82) \times 10^{-5}$ mol dm⁻³. All solutions were freshly prepared each day, and their absorbances as well as those of their mixtures were measured within 5 hr. All the operations were performed in an air-conditioned room ($\sim 22^\circ\text{C}$) in subdued light. At the beginning of the measurements of a set of solutions, the spectra of pure compounds were recorded to detect any change.

Spectrophotometric measurements were made on a Shimadzu UV-200 S double beam spectrophotometer, using a rectangular cell of 1 cm pathlength and solvent as the blank. The absorption spectral bands of the semiquinone anion obtained due to the interaction between chloranil/bromanil and the hexacyanometalate(4-) ions were observed at wavelengths longer than those of λ_{max} of individual pure components at concentrations identical to those used in the mixture^{4,15}. The absorbances were measured after ~ 5 min of placing the cell in a thermostated cell holder for allowing the equilibrium to be

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attained. The accuracy of the measurements was ± 0.01 absorbance unit.

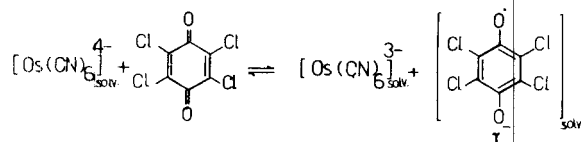
Results and Discussion

Interaction of potassium hexacyanoosmate(II) with chloranil and bromanil

For hexacyanoosmate(II)-halonil mixtures in 20-70% (vol./vol.) aqueous dimethyl sulphoxide media, new strong electronic absorption spectral bands are immediately formed after mixing the constituents (Fig. 1 and Table 1). The positions of the new bands are not affected by the solvent polarity, but the absorbance diminishes with increasing the water content of the medium.

Several studies^{4,9,10,16} have shown that in solvents of high ionizing power the major absorption band of chloranil (288 nm) is red-shifted on complex formation, a phenomenon particularly marked with strong donors⁹. The shift of the absorption is due to the formation of the negative semiquinone ion⁴. The resultant spectrum is, therefore, due to contributions from both neutral and ionized forms (Fig. 1).

In aqueous dimethyl sulphoxide, the solvation of the hexacyanoosmate(II) ion and halonil molecule immediately causes almost complete electron-transfer in the ground electronic state, i.e., the result is the formation of the negative semiquinone ion. In hexacyanoosmate(II)-chloranil system, for example, the absorption bands at 424 and 451 nm, which have been assigned to the negative semiquinone ion (I) derived from chloranil, are observed (Fig. 1).



This assignment is supported by the facts that absorption positions are not affected by changes in the medium polarity or the nature of the metal in the $[\text{M}(\text{CN})_6]^{4-}$ ions (Table 1), and the absorption spectra are similar to that of the product obtained by the reaction of chloranil with sodium iodide¹⁷.

The electronic absorption spectrum of $[\text{Os}(\text{CN})_6]^{3-}$ ions shows two bands at 261 and 283 nm¹⁸ and has no absorption in the range 400 to 460 nm.

The stoichiometry of the electron-transfer interaction (2) between the donor hexacyanometalate(4-)

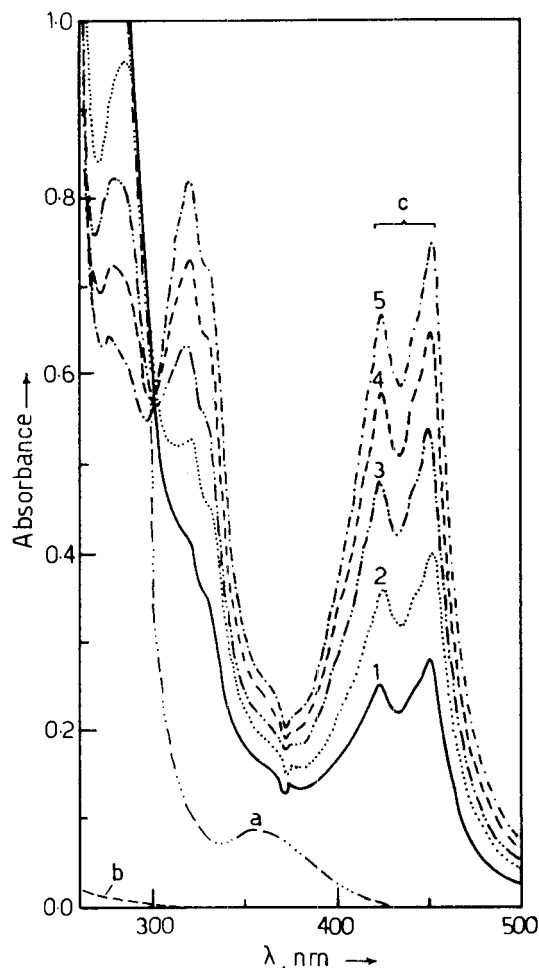


Fig. 1—The electronic absorption spectra in 20% (vol./vol.) aqueous dimethyl sulphoxide at 27°C of (a), chloranil (9.5×10^{-5} mol dm⁻³); (b), $\text{K}_4[\text{Os}(\text{CN})_6]$ (7.84×10^{-5} mol dm⁻³); and (c), chloranil (9.5×10^{-5} mol dm⁻³) to which the following amounts of $\text{K}_4[\text{Os}(\text{CN})_6]$ (mol dm⁻³ $\times 10^{-5}$) were added: (1), 2.47; (2), 3.71; (3), 5.21; (4), 6.49; (5), 7.84×10^{-5} mol dm⁻³.

Table 1—Absorption maxima ($\lambda_{\text{max}}^{\text{A-}}$), molar extinction coefficients ($\epsilon_{\text{max}}^{\text{A-}}$) and equilibrium constants (K_c) obtained for the interactions between chloranil/bromanil and the hexacyanometalate (4-) ions in aqueous dimethyl sulphoxide media at 27°C

Medium (%, vol./vol.)	Acceptor (A)	Donor [D] ⁴⁻	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_5 (nm)	$K_c \times 10^{-3}$ (dm ³ mol ⁻¹)	$\epsilon_{\text{max}}^{\text{A-}} \times 10^{-3}$ (cm ² mol ⁻¹)
20% aqueous	Bromanil	$[\text{Os}(\text{CN})_6]^{4-}$	408sh	—	424	—	454	4.51	57.1
DMSO	Chloranil	$[\text{Os}(\text{CN})_6]^{4-}$	404sh	418sh	424	444sh	451	6.24	33.3
	Chloranil	$[\text{Ru}(\text{CN})_6]^{4-}$	404sh	418sh	426	445sh	451	4.83	33.3
	Chloranil	$[\text{Fe}(\text{CN})_6]^{4-}$	404sh	418sh	425	445sh	451	7.26	33.3
50% aqueous	Chloranil	$[\text{Fe}(\text{CN})_6]^{4-}$	405sh	420sh	426	447sh	451	22.65	22.5
DMSO									
70% aqueous	Chloranil	$[\text{Fe}(\text{CN})_6]^{4-}$	407sh	422sh	427	449sh	451	32.90	15.4
DMSO									

ion (D^{4-}) and the acceptor halonil molecule (A),
 $dD^{4-} + aA \rightleftharpoons D_d^{3-} + A_a^-$... (2)

was determined applying Eq. (3)^{7b}:

$$A_{\lambda}^{A^-} = K_c \epsilon_{\lambda}^{A^-} [D^{4-}]^d [A]^a \quad \dots (3)$$

where $A_{\lambda}^{A^-}$ and $\epsilon_{\lambda}^{A^-}$ are the absorbance and the molar absorptivities, respectively, of the negative semiquinone ion (I) at wavelength λ , and K_c is the equilibrium constant. A log-log plot of $A_{\lambda}^{A^-}$ versus concentration of one component, keeping that of the other constant, proved that under the present experimental conditions the reaction stoichiometric ratio was one.

Since the absorption spectra slowly change with time due to air oxidation¹⁹, the reaction equilibrium constants were determined from the spectra immediately recorded after mixing the reactants.

To study the reaction equilibrium constants (K_c), we have the following equations:



$$K_c = \frac{x}{(a-x)(b-x)} \quad \dots (6)$$

Equation (6) may be rearranged to obtain Eq. (7),

$$\frac{a}{x} = \frac{1}{K_c} \cdot \frac{1}{b} + \frac{a}{b} + 1 - \frac{x}{b} \quad \dots (7)$$

Since the absorbance in the region of the new $\lambda_{\max}$ is due to the semiquinone anion (A^-) (Fig. 1), and the solution is of 1 cm path-length, according to Eq. (5), the molar absorptivity of the anion A^- at wavelength λ is given by Eq. (8),

$$\epsilon_{\lambda}^{A^-} = \frac{A_{\lambda}^{A^-}}{x} \quad \dots (8)$$

Combining Eqs (7) and (8), we get

$$\frac{a}{A_{\lambda}^{A^-}} = \frac{1}{K_c \epsilon_{\lambda}^{A^-}} \cdot \frac{1}{b} + \frac{a}{b \epsilon_{\lambda}^{A^-}} + \frac{1}{\epsilon_{\lambda}^{A^-}} - \frac{x}{b \epsilon_{\lambda}^{A^-}} \quad \dots (9)$$

Since $b \gg x$, using the concentration of the electrons (b) as that of the hexacyanometalate(4-) ion as an approximation, it is possible to neglect the last term in the right hand side of Eq. (9)²⁰, so that

$$\frac{a}{A_{\lambda}^{A^-}} = \frac{1}{b} \left(\frac{1}{K_c \epsilon_{\lambda}^{A^-}} + \frac{a}{\epsilon_{\lambda}^{A^-}} \right) + \frac{1}{\epsilon_{\lambda}^{A^-}} \quad \dots (10)$$

For a series of solutions of constant a and varying b , a plot of $(a/A_{\lambda}^{A^-})$ against $(1/b)$ should be linear. The intercept of the line on the ordinate gives $(\epsilon_{\lambda}^{A^-})^{-1}$ of the semiquinone anion A^- and the slope is equal to

$[(K_c \cdot \epsilon_{\lambda}^{A^-})^{-1} + a(\epsilon_{\lambda}^{A^-})^{-1}]$, so that K_c and $\epsilon_{\lambda}^{A^-}$ can be evaluated. Plots of Eq. (10) for chloranil-/bromanil-hexacyanoosmate(II) mixtures are represented in Fig. 2 while the K_c and $\epsilon_{\lambda}^{A^-}$ values are given in Table 1.

From Table 1, it is clear that chloranil interacts more strongly with the hexacyanometalate(4-) ions. This can be attributed to the higher electron withdrawing character of the chlorine atoms which increases to some extent the acceptor ability of the chloranil molecule relative to the bromanil, due to a flow of more electronic charge from the 1,4-benzoquinone nucleus to the chlorine atoms.

Interaction of chloranil with the hexacyanometalate(4-), $K_4[M(CN)_6]$, where $M = Fe, Ru$ and Os

Plots of Eq. (10) gave linear slopes which could be taken as an evidence for the validity of Eqs 5 and 10 (Fig. 2). The K_c and $\epsilon_{\lambda}^{A^-}$ values are given in Table 1.

In 20% (vol./vol.) aqueous dimethyl sulphoxide it is evident that the ability of chloranil molecule to accept an electron from the hexacyanometalate(4-) ion depends on the redox potentials²¹ of the $[M(CN)_6]^{4-/3-}$ ions and follows the order: $Fe(II) > Os(II) > Ru(II)$ (Table 1). It is interesting to

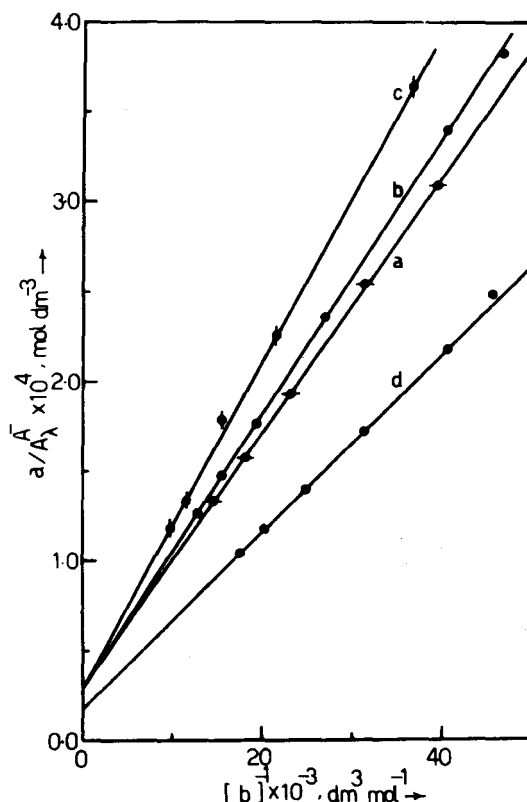


Fig. 2—Plots of $a/A_{\lambda}^{A^-}$ versus $[b]^{-1}$ for 20% (vol./vol.) aqueous dimethyl sulphoxide solution containing fixed [halonil] and different concentrations of $[M(CN)_6]^{4-}$ ions at 27°C. The systems are: (a), $K_4[Fe(CN)_6]$ -chloranil; (b) $K_4[Os(CN)_6]$ -chloranil; (c), $K_4[Ru(CN)_6]$ -chloranil; and (d), $K_4[Fe(CN)_6]$ -bromanil system.

find that the values of the equilibrium constants, K_c , are directly proportional to the redox potentials²¹ of the hexacyanometalate(4-) ions. The increase in the negative $E_{1/2}$ value of the $[M(CN)_6]^{4-/3-}$ ion will decrease its electron donor ability and consequently lead to a smaller K_c value.

Table 1 also shows that the molar absorbance of the negative semiquinone ion (I), ϵ_{λ}^- , has a definite value ($33.3 \times 10^{-3} \text{ cm}^2 \text{ mol}^{-1}$) in 20% aqueous dimethyl sulphoxide which is independent of the hexacyanometalate(4-) ion.

Solvent effects

The interaction of chloranil with hexacyanoferrate(II) ion, $[\text{Fe}(\text{CN})_6]^{4-}$, was investigated in aqueous sulphoxide media with varying amounts of water content (from 20 to 70%, vol./vol.) with a view to investigate the influence of the medium composition on the electron-transfer process.

In the solvent mixtures used, it is evident that the ability of chloranil molecules to accept an electron from the hexacyanoferrate(II) ion strongly depends on the medium composition. The value of the equilibrium constants (K_c) increases greatly with increasing water content of the medium. The increase in the dielectric constant of the medium with increasing water content facilitates to a great extent the donor and acceptor abilities of the interacting species and consequently higher K_c values are obtained.

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