

Interaction of dimethyl sulphoxide with chloranil by ESR and optical methods

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Abstract. The molecular charge-transfer absorption bands have been observed in solution of dimethyl sulphoxide (DMSO) and tetrachloro-*p*-benzoquinone (chloranil) in chloroform and cyclohexanone. The stability constant, the thermodynamic parameter of the complex and the extinction co-efficient of CT bands at 350 nm in chloroform and 360 nm in cyclohexanone have been estimated on the assumption of the 1:1 complex formation. Detection of ESR signal of the solution of chloranil in pure DMSO ($g \approx 2$) indicates the formation of chloranil radical anion, the precursor being the charge-transfer complex, which dissociates partly in high dielectric constant DMSO.

Keywords. Charge transfer; electron spin resonance; optical property.

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1. Introduction

A series of studies (Slifkin 1964; Beukers and Szent 1962) have been made on the charge-transfer interactions of chloranil as electron acceptor with DMSO as donor. In view of the importance of chloranil as a model for biological quinones, studies on its complexation have been extended to many drugs, notably phenothiazines as donors, but in each case only the chloranil anion spectra were observed without any indication of charge-transfer (CT) band (Saucin *et al* 1968). Similar results have been obtained for other groups of bio-molecules (Slifkin 1961, 1973). Various purines and pyrimidines on mixing with chloranil in DMSO slowly develop a red colour (Machmer and Duchesne 1965). The molecular mechanism of DMSO on TCNE has been thoroughly studied by optical and ESR technique by Stewart *et al* (Stewart 1966). The object of the present investigation is precisely to find the interaction of DMSO, if any, with chloranil.

2. Experimental

DMSO and the solvents used were of the spectroscopic grade product of E-Merck, Germany. The chloranil was prepared by prescribed method (Arnold and Collins 1942) and was purified by vacuum distillation and crystallization from benzene. The measurements of absorption spectra were taken with Cary D-17 spectrophotometer. Difference spectra were taken using two separate cells, one containing chloranil,

DMSO and solvent, the other with DMSO and solvent. The electron spin resonance spectrum of chloranil in DMSO was taken in a home-made X-band ESR spectrometer employing 100 kHz field-modulation. The field calibration was done with the help of proton-resonance side-band technique (Sanyal and Roy 1982). Infrared spectra of the solution of chloranil in DMSO were taken in Beckmann IR20 spectrophotometer.

3. Results and discussion

In the present work the absorption spectra of chloranil and DMSO in chloroform show a peak at 350 nm for low donor and acceptor concentration, and for higher

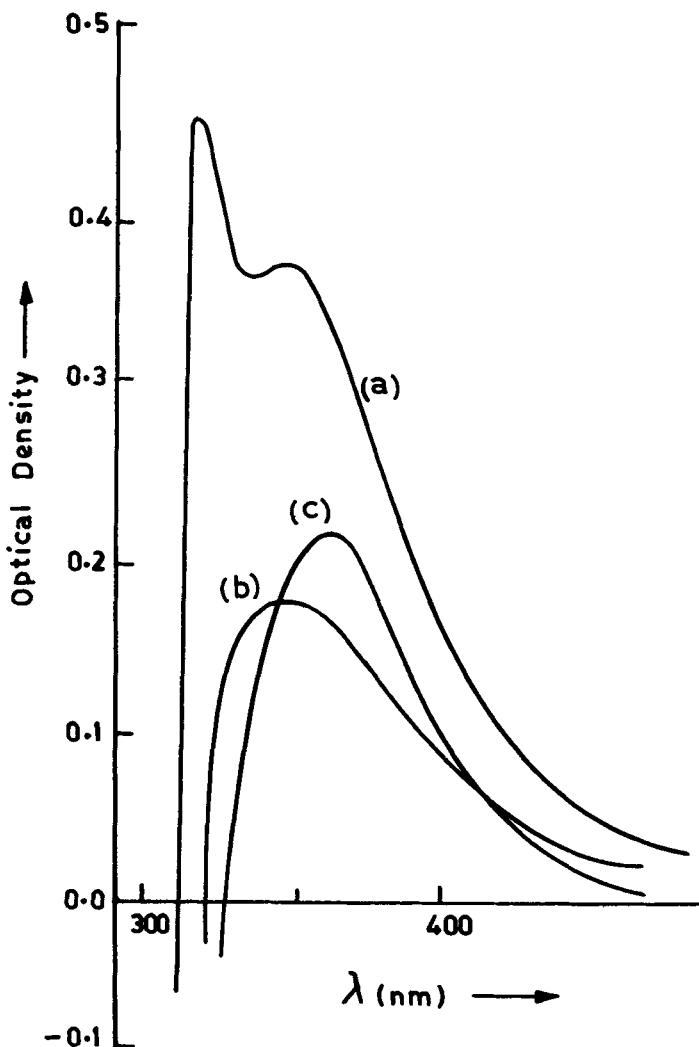


Figure 1. Absorption spectra (a) In chloroform $[A] = 6.6 \times 10^{-4}$ (M/L), $[D] = 2.35$ (M/L) (b) In chloroform $[A] = 3 \times 10^{-5}$ (M/L), $[D] = 1.41$ (M/L) (c) In cyclohexanone $[A] = 6.6 \times 10^{-4}$ (M/L), $[D] = 1.41$ (M/L).

concentration an extra peak at 310 nm appears. On the other hand, a single absorption peak at 360 nm appears for chloranil and DMSO in the solvent cyclohexanone. This behaviour is shown in figure 1. The extra peak at 310 nm (figure 1a) for higher concentration seems to have arisen from the broadening of the chloranil absorption due to interaction with DMSO. It is to be noted that the absorption spectrum of chloranil anion has been reported to have maxima at 315, 330, 427 and 455 nm (Slifkin 1964). The spectrum of the complex of chloranil with aminoacids in ethanol shows a peak in between 350 nm and 390 nm depending on pH (Birks and Slifkin 1963). The 350 nm peak in chloroform or the 360 nm peak in cyclohexanone (as cited above) do not correspond to the chloranil anion. Unlike the earlier observations the solution of chloranil in DMSO (concentration of chloranil 7×10^{-2} mol/litre) exhibit ESR spectrum (figure 2) with $g \approx 2$ and ΔH (linewidth) ≈ 4.96 gauss.

The equilibrium constant for complex-formation was evaluated using 350 nm and 360 nm peak from the relation (Benesi and Hildebrand 1949)

$$\frac{[A]l}{\log I_0/I} = \frac{1}{K_c \epsilon_{CT}} \times \frac{1}{[D]} + \frac{1}{\epsilon_{CT}} \quad (1)$$

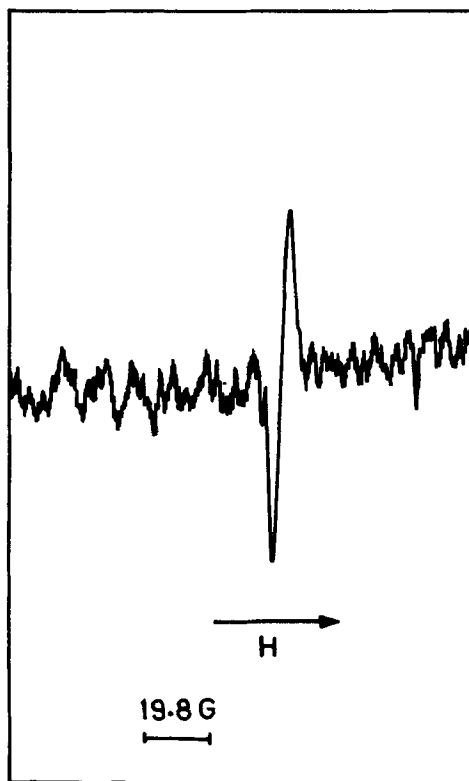


Figure 2. Typical ESR spectrum of the solution of chloranil in DMSO.

Table 1. Parameters of the charge-transfer complex.

Solvent	λ_{\max}	K_c litre/mol	ϵ_{CT}	ΔH_0 kcal/mol
Chloroform	350	0.2	1000 (at 28°C)	-0.64
Cyclohexanone	360	0.25	980 (at 28°C)	-0.69
* Carbon tetrachloride	394	4.41 (at 20°C)	—	-3.5

* Values calculated from Slifkin (1969)

and the enthalpy of dissociation of the complex was computed from the expression

$$\frac{d}{dT}(\ln K_c) = \frac{-\Delta H_0}{RT^2} \quad (2)$$

where $[A]$ and $[D]$ are respectively molar concentrations of acceptor and donor molecules, K_c is the equilibrium constant for 1:1 complex, ϵ_{CT} is the molar extinction co-efficient of the complex. ΔH_0 is the change of enthalpy, others have usual meaning. The results are given in table 1. ϵ_{CT} values in table 1 are for 28°C. No shift of λ_{\max} with change of temperature is noted as shown in figure 4. Infrared spectra of chloranil-DMSO shows a red-shift of -SO stretching frequency from 1320 to 1290 cm^{-1} and of carbonyl band from 1690 to 1650 cm^{-1} but a new band appears at 1380 cm^{-1} (figure 3) which is possibly the red-shifted band of -C=C- of pure chloranil (Slifkin 1970) which occurs at 1572 cm^{-1} . The observed peaks obey not only Benesi-Hildebrand equation but are also temperature reversible (figure 4) and as such they are treated as charge-transfer bands with the possibility of 1:1 complexation as evidenced from the above infrared spectra of the same. Therefore, DMSO is not a non-interacting solvent as regards chloranil and is most probably donating n -electron from oxygen into the antibonding orbital of chloranil. It therefore appears that decrease in bond order of the molecule is detected both in the carbonyl as well as -C=C- bands. These complexes are not wholly dative as the case of phenothiazine complexes, (Matsunaga 1964) where carbonyl IR frequency is shifted to 1580 cm^{-1} . In the present case, dielectric constant of DMSO being high, a small fraction of the complex ionizes. The resulting acceptor anion gives rise to ESR signal and the corresponding donor cation gets solvated in DMSO and thereby its ESR signal is not observable.

The oxygen-free DMSO-chloranil solution through which nitrogen gas is passed does not show any colouration even in a month. In presence of oxygen the ESR signal has been observed to decay slowly and a red colouration develops in the DMSO-chloranil solution. The destruction of chloranil by DMSO as reported by Slifkin (Slifkin 1964) is then a secondary process involving chloranil anion and perhaps oxygen also.

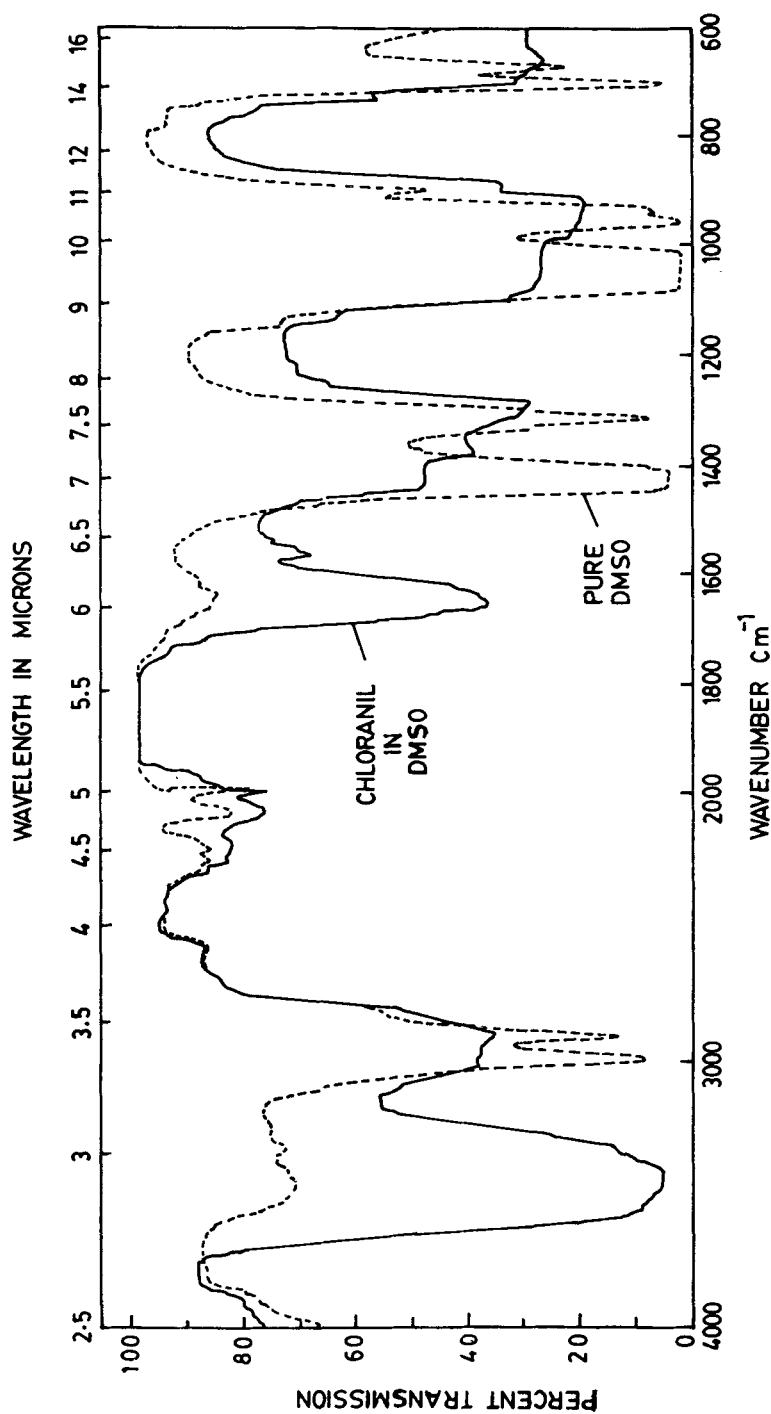


Figure 3. Typical IR spectra.

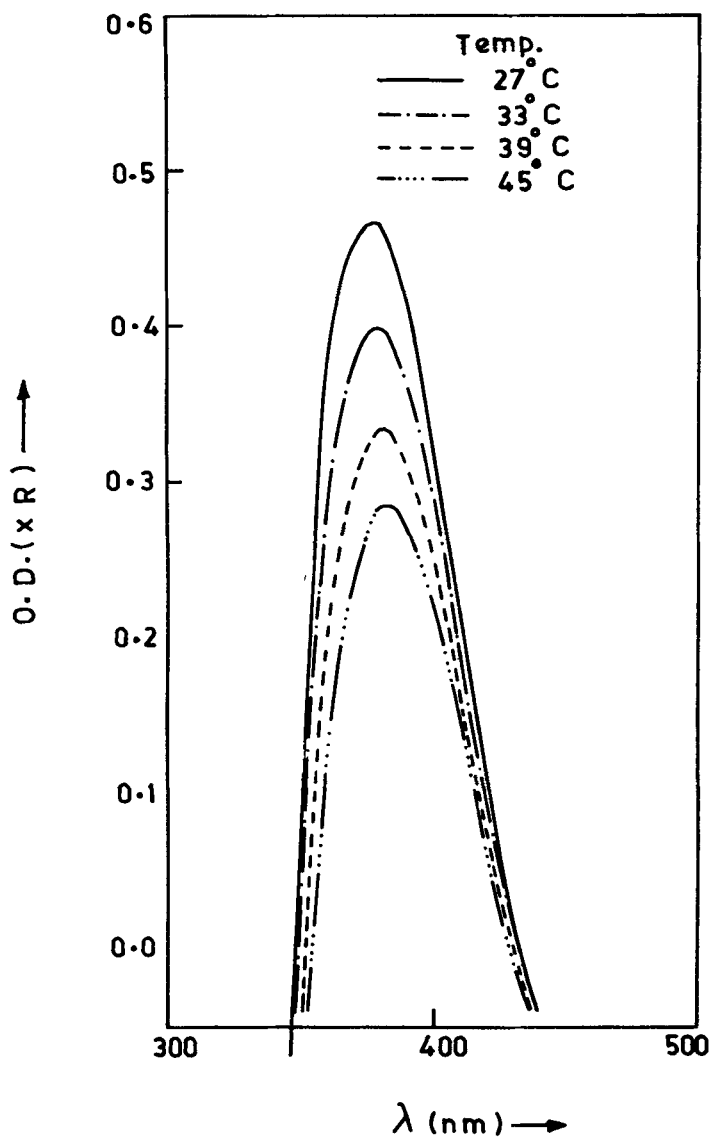


Figure 4. Variation of O.D with temperature $R = 0.5$.

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