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Effects of Electron Donors on the Photodecomposition of Menadione in Aqueous Solution. IV.[1] Charge Transfer Absorption Bands of the Complexes between Menadione and either Caffeine or Ethyl *p*-Aminobenzoate

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In previous papers, it was reported that menadione formed complexes with various electron donrs in aqueous systems, and that the driving force of the complex formation was due to the charge transfer force. However, the charge transfer absorption bands of the complexes were not recognized completely in the above systems.

In the present paper, the charge transfer absorption bands of the complexes between menadione and either caffeine or ethyl *p*-aminobenzoate were determined in chloroform, and energies of the charge transfer absorption bands were compared with those between better electron donors and menadione, or between better electron acceptors and either caffeine or ethyl *p*-aminobenzoate.

Consequently, it was concluded that the indistinct charge tranfser absorption bands of the complexes between menadione and either caffeine or ethyl *p*-aminobenzoate in aqueous system are responsible for lower electronic affinity of menadione, for higher ionization potentials of caffeine or ethyl *p*-aminobenzoate and for lower solubilities of caffeine or ethyl *p*-aminobenzoate.

In previous papers of this series,[3,4] it was reported that menadione was stabilized by the complex formation with various electron donors in aqueous solution, and according to the calculation on the stabilization energies of the complexes, it has been shown that the driving force of the complexes was due to the charge transfer force.[5] However, the charge transfer absorption bands of the complexes had not been recognized definitely in aqueous system as reported in a previous paper.[3]

In this connection, it may be thought to be caused by following reasons: i) menadione was not considered to be a better electron acceptor such as chloranil or 1,4-naphthoquinone, ii) various electron donors used in preceding paper were not considered to be a better electron donor such as N,N-dimethylaniline or N,N-diethylaniline and iii) solubilities of electron donors were lower in the case of aqueous solution.

In the present paper, measurements of the charge transfer absorption bands of the complexes between menadione and either caffeine or ethyl *p*-aminobenzoate were attempted in chloroform, and so energies of the charge trasnfer absorption bands of the complexes were compared with those of the complexes between better electron donors and menadione, or between better electron acceptors and either caffeine or ethyl *p*-aminobenzoate.

Experimental

Materials——Chloroform used was of G.R. grade-chemical, purchased from Wako Junyaku Co., Ltd. It was washed four times with an equal volume of distilled water, dried over calcium chloride, and distilled

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[1] Part III: *Chem. Pharm. Bull.* (Tokyo), **16**, 1 (1968).
[2] Location: *Takada, Toshima-ku, Tokyo.*
[3] S. Hata, K. Mizuno, and S. Tomioka, *Chem. Pharm. Bull.* (Tokyo), **15**, 1791 (1967).
[4] S. Hata, K. Mizuno, and S. Tomioka, *Chem. Pharm. Bull.* (Tokyo), **15**, 1796 (1967).
[5] S. Hata, K. Mizuno, and S. Tomioka, *Chem. Pharm. Bull.* (Tokyo), **16**, 1 (1968).

under nitrogen atmosphere. All amines were obtained commercially and purified according to the literature.

1,2–Naphthoquinone and 1,4–naphthoquinone were of G.R. grade–chemicals, purchased from Tokyo Kasei Co., Ltd., and were used without further purification. Chloranil and *p*–benzoquinone were also of E.P. grade–chemicals, purchased from Tokyo Kasei Co., Ltd., and were used after recrystallization. Menadione, caffeine and ethyl *p*–aminobenzoate were the same as described in a previous paper.$^{3)}$

Measurements of Absorption Spectra——The absorption spectra were measured with a Hitachi photoelectric spectrophotometer EPU–2A, equipped with thermospacers which maintained the cell compartments at 24±0.1°, and the cell length was 10 mm. Concentrations of various electron donors and acceptors are shown in Table I. The results of the measurements are shown as differential spectra in Fig. 1.

Table I. Concentrations (M/liter) of Various Electron Donors and Acceptors used for the Measurements of Charge Transfer Absorption Bands

Donor / Acceptor	N,N–Diethyl-aniline (1.55)	N,N–Dimethyl-aniline (1.57)	N–Ethyl-aniline (1.58)	N–Methyl-aniline (1.84)	Ethyl *p*–aminobenzoate (1.21)	Caffeine (0.77)
Chloranil	1.30×10^{-4}	1.30×10^{-4}	1.30×10^{-4}	1.30×10^{-4}	1.30×10^{-4}	1.30×10^{-4}
p–Benzoquinone	—	1.38×10^{-3}	—	—	1.38×10^{-3}	1.15×10^{-4}
1,2–Naphthoquione	—	2.52×10^{-4}	—	—	2.52×10^{-4}	1.26×10^{-4}
1,4–Naphthoquinone	—	2.52×10^{-4}	—	—	2.52×10^{-4}	1.26×10^{-4}
Menadione	1.74×10^{-3}	1.74×10^{-3}	1.74×10^{-3}	1.74×10^{-3}	1.74×10^{-4}	1.74×10^{-4}

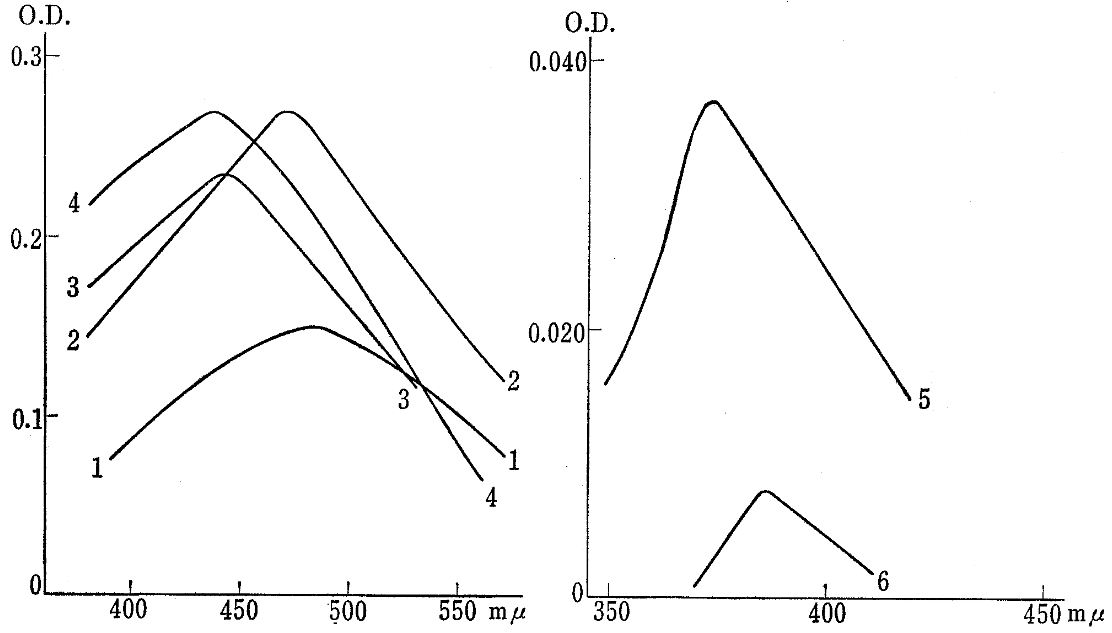

Fig. 1. Charge Transfer Absorption Bands of the Complexes between Menadione and Various Electron Donors in Chloroform

1: N,N–Diethylaniline 2: N,N–Dimethylaniline 3: N–Ethyl–aniline
4: N–Methylaniline 5: Ethyl *p*–aminobenzoate; 6: Caffeine

Results and Discussion

The charge transfer absorption bands of the complexes between menadione and various electron donors such as N,N–dimethylaniline, caffeine and ethyl *p*–aminobenzoate *etc.* are shown in Fig. 1. The charge transfer absorption bands are also brought about by the complexes between other electron donors and acceptors used in the present study, and the charge transfer absorption maxima of those complexes were determined as tabulated in Table II.

Those observations revealed that menadione showed the charge transfer absorption bands by the complexes formation with either caffeine or ethyl *p*–aminobenzoate in chloroform.

Table II. Values (in mμ) for the Position of the Charge Transfer Absorption Bands of the Complexes between Various Electron Donors and Acceptors in Chloroform

Acceptor / Donor	Chloranil	*p*-Benzoquinone	1,2-Naphthoquinone	1,4-Naphthoquinone	Menadione
N,N-Diethylaniline	755	—	—	—	480
N,N-Dimethylaniline	660	521	503	485	471
N-Ethylaniline	605	—	—	—	442
N-Methylaniline	605	—	—	—	439
Ethyl *p*-aminobenzoate	525	410	456	423	373
Caffeine	425	402	400	405	386

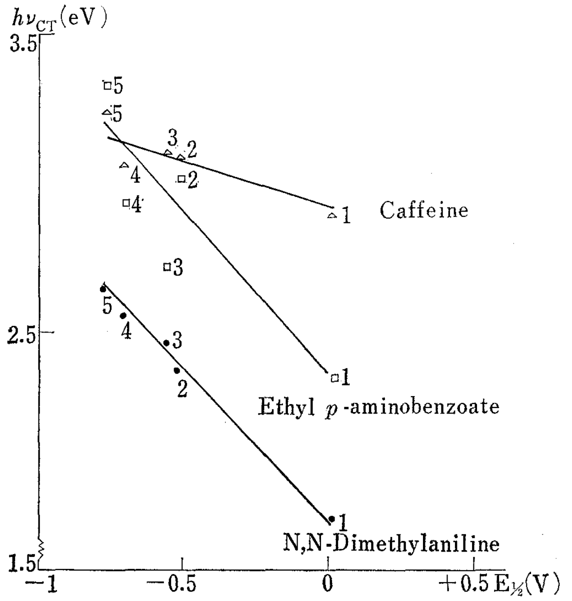

Fig. 2. Relation between the Energy ($h\nu_{CT}$) of the Charge Transfer Absorption Bands in Chloroform and the Half Wave Potential ($E_{1/2}$) of the Aceptor

1: Chloranil 2: *p*-Benzoquinone
3: 1,2-Naphthoquinone 4: 1,4-Naphthoquinone
5: Menadione

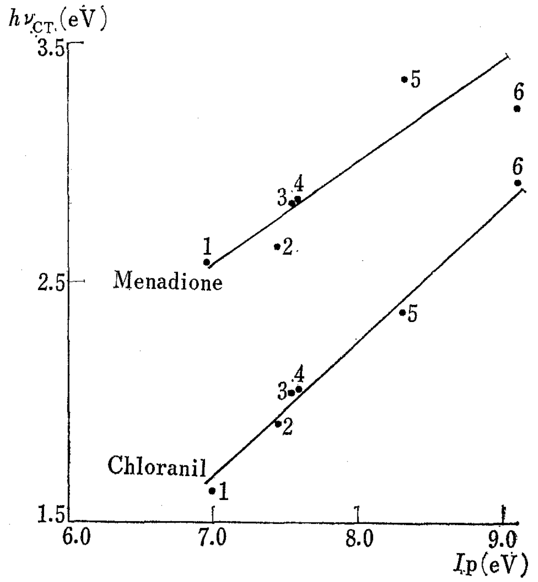

Fig. 3. Relation between the Energy ($h\nu_{CT}$) of the Charge Transfer Absorption Bands in Chloroform and the Ionization Potential (I_p) of the Donor

1: N,N-Diethylaniline 2: N,N-Dimethylaniline
3: N-Ethylaniline 4: N-Methylaniline
5: Ethyl *p*-aminobenzoate[a] 6: Caffeine[a]

[a] Obtained by the equation $\varepsilon=\alpha+\lambda_{h.o.}\beta$,[1] as $\alpha=-7.2$ eV and $\beta=-3.0$ eV, respectively. The parameters of coulomb and resonance integrals for substituent groups are the same as the values cited in a previous paper.[1]

However, the energies of charge transfer absorption bands of the complexes are not so low as those of the complexes with other electron donors such as N,N-dimethylaniline.

Then, the relationships between the energies of the charge transfer absorption bands and the half wave potential of the acceptor[6] or the ionization potential of the donor[7] were investigated, being shown in Fig. 2 and 3, respectively.

From these results, it is to be noted that the capacity of charge tranfer complex formation of menadione is weaker than those of other electron acceptors such as chloranil, and that the capacities of charge transfer complex formation of caffeine and ethyl *p*-aminobenzoate

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[6] M.E. Peover, *Nature*, **191**, 702 (1961); *idem*, *Trans. Faraday Soc.*, **58**, 1656 (1962).
[7] P.G. Farrell and J. Newton, *J. Phys. Chem.*, **69**, 3506 (1965).

are also weaker than those of other electron donors such as N,N–dimethylaniline. And, it may be assumed that such a fact is as the same in aqueous systems in the sense of relative relation. Consequently, it will be concluded that the indistinct charge transfer absorption bands of the complexes between menadione and either caffeine or ethyl *p*–aminobenzoate in aqueous systems are responsible for lower electronic affinity of menadione, for higher ionization potentials of caffeine or ethyl *p*–aminobenzoate and for lower solubilities of caffeine or ethyl *p*–aminobenzoate.