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Charge Transfer Absorption Bands of the Complexes between Various Electron Donors and Menadione in Aqueous Solution

SHUN-ICHI HATA and SUIICHI TOMIOKA

Research Laboratories, Chugai Pharmaceutical Co., Ltd.[1]

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In previous papers,[2,3] it was reported that menadione was stabilized by the complex formation with various electron donors in aqueous solution, and that according to the calculation on the stabilization energies of the complexes, the driving force of the complexes was shown to be due to the charge transfer force.[4] However, the charge transfer absorption bands of the complexes were not recognized definitely in aqueous solution as reported in a previous paper.[2]

In the present paper, measurements of the charge transfer absorption bands of the complexes between menadione and various electron donors were attempted in aqueous solution, and the energies of the charge transfer absorption bands of the complexes were determined. Then, the relationships between the energies of the charge transfer absorption bands and various constants related to the complex formation, reported previously,[2,3,4] were discussed.

Experimental

Materials——Menadione and various electron donors used in this paper were the same as described in a previous paper.[2]

Measurements of Absorption Spectra——The absorption spectra were measured with a Hitachi photoelectric spectrophotometer EPU-2A, equipped with thermospacers to maintain the cell compartments at 24 ± 0.1°, and the cell length was 10 mm. The sample solutions were prepared by dissolving in phosphate buffered solution (N/15) of pH 7.0. The results of the measurements are shown in Fig. 1 as differential spectra.

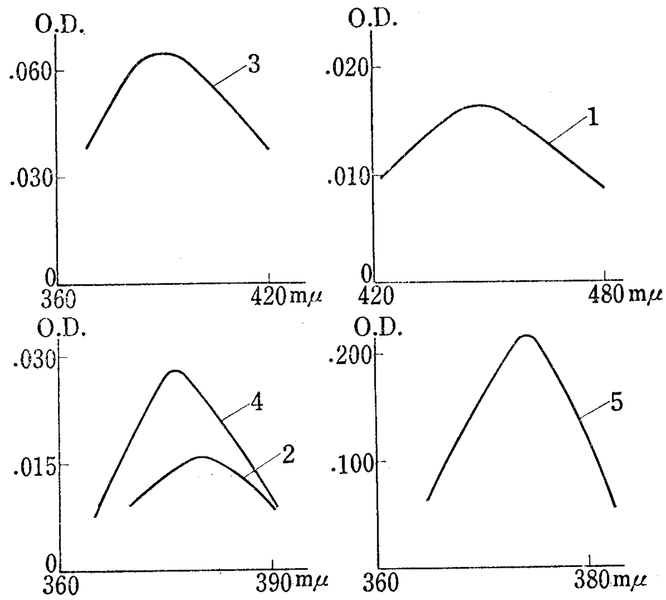

Fig. 1. Charge Transfer Absrotpion Bands of the Complexes between Menadione (6.97×10^{-4}M/liter) and Various Electron Donors in Aqueous Solution

1: β-hydroxynaphthoic acid (5.53×10^{-3}M/liter); 2: sodium salicylate (1.25M/liter); 3: caffeine (1.03×10^{-1}M/liter); 4: nicotinamide (1.64M/liter); 5: sodium dehydroacetate (7.21×10^{-1}M/liter)

Results and Discussion

The charge transfer absorption bands of the complexes between menadione and various electron donors such as β-hydroxynaphthoic acid, caffeine and nicotinamide and so on are shown in Fig. 1, and the energies of the charge

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

transfer absorption maxima of those complexes ($h\nu_{CT}$) were determined as tabulated in Table I.

Table I. Energy of the Charge Transfer Absorption Band

No.	Donor	Maxima (mμ)	$h\nu_{CT}$ (e.V.)
1	β-Hydroxynaphthoic acid	445	2.79
2	Salicylic acid	380	3.26
3	Caffeine	390	3.18
4	Nicotinamide	376	3.30
5	Dehydroacetic acid	374	3.32

Those observations revealed that menadione showed the charge transfer absorption bands by the complex formation with various electron donors in aqueous solution. Then, the relationships between the energies of the charge transfer absorption bands and the parameter for energy levels of the highest occupied molecular orbitals of various electron donors ($\lambda_{h.o.}$) or the stabilization energy (δE) of the complex formation reported in previous papers,[2,4] were investigated. The results thus obtained are shown in Figs. 2 and 3.

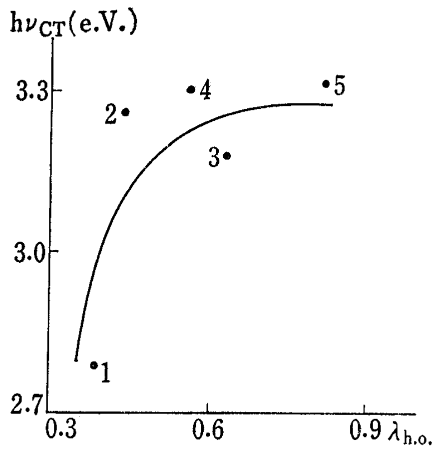

Fig. 2. Relation between $h\nu_{CT}$ and the Parameter for Energy Levels of the Highest occupied Molecular Orbitals (λ_{ho})

1: β-hydroxynaphthoic acid; 2: salicylic acid; 3: caffeine; 4: nicotinamide; 5: dehydroacetic acid

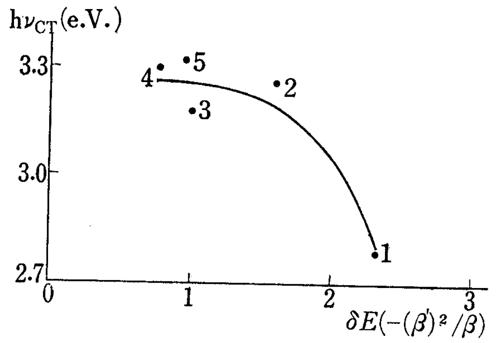

Fig. 3. Relation between $h\nu_{CT}$ and Stabilization Energy (δE)

1: β-hydroxynaphthoic acid; 2: salicylic acid; 3: caffeine; 4: nicotinamide; 5: dehydroacetic acid

Expectedly, the energies of the charge transfer absorption bands tend to be increased by the addition of such a substance as dehydroacetic acid or nicotinamide which is grouped as weaker donors.

Next, the relationships between the energies of the charge transfer absorption bands and the free energy change or the enthalpy change of the complex formation reported in the previous paper,[2] were also investigated. Being shown in Figs. 4 and 5, the free energy change and the enthalpy change in the complex formation are roughly parallel to the energies of the charge transfer absorption bands. In addition, Fig. 6 shows that stability of menadione tends to be increased by the decrease of the energies of charge transfer absorption bands.

Hence, it is again concluded decisively by these facts that suppression of the photodecomposition of menadione with various electron donors in aqueous solution[3] is mainly due to the charge transfer complex formation between them.

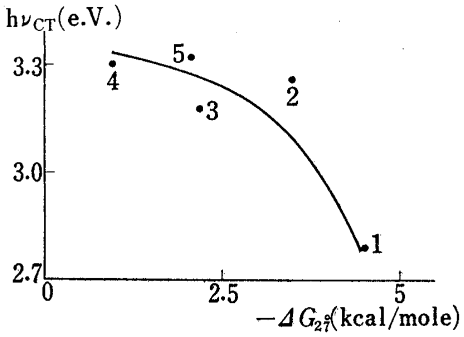

Fig. 4. Relation between $h\nu_{CT}$ and Free Energy Change ($\Delta G_{27°}$)

1: β-hydroxynaphthoic acid; 2: salicylic acid; 3: caffeine; 4: nicotinamide; 5: dehydroacetic acid

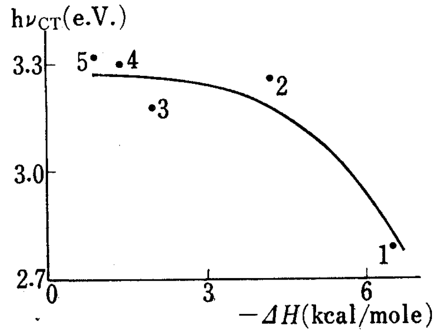

Fig. 5. Relation between $h\nu_{CT}$ and Enthalpy Change (ΔH)

1: β-hydroxynaphthoic acid; 2: salicylic acid; 3: caffeine; 4: nicotinamide; 5: dehydroacetic acid

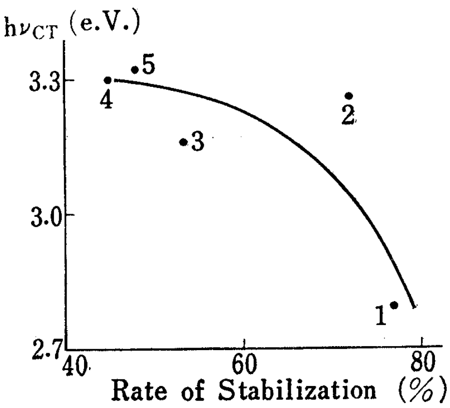

Fig. 6. Relation between $h\nu_{CT}$ and Rate of Stabilization

1: β-hydroxynaphthoic acid; 2: salicylic acid; 3: caffeine; 4: nicotinamide; 5: dehydroacetic acid