Tetrahedron Letters No. 27, pp. 2495-2498, 1971. Pergamon Press. Printed in Great Britain.

CHARGE TRANSFER COMPLEXES OF POLYENE WITH CHLORANIL

Hirotada Iida, Tetsuo Nogami, Takashi Sawahata, Akio Noguchi and Kazutoshi Yamada
Department of Synthetic Chemistry, Chiba University,
1-Yayoicho, Chiba, Japan

(Received in Japan 15 April 1971; received in UK for publication 2 June 1971)

The complexes of alkenes which have been studied most extensively are those in which silver ion functions as the acceptor[1]. A qualitative relationship existing between the biochemical importance of the polyene group and its electron donor properties has often been suggested[2]. However, the charge transfer (CT) interaction between π-electron acceptor and polyene has never been explained.

We now wish to report on the CT-interaction of polyenes-chloranil complexes. The variation of the concentration between acceptor and donors as observed in the absorption spectrum gives bond ratio[3], equilibrium constant, molar extinction coefficient[4], and thermodynamic parameters[5] in those complexes. The present observation on the CT-behavior of polyene is thought to be consistent with the possibility that the natural polyene may be involved in electron transfer relation in vivo.

Eleostearic acid (EA) was obtained by the saponification of tung oil. Allo-ocimene (AO) and vitamin A acetate (VA) were commercially available. Chloranil (CA) and tetrahydrofurane (THF) were purified by usual methods. The absorption spectra of CT-complexes were measured in THF in the interval -20 ~ -70°C. A HITACHI RECORDING SPECTROPHOTOMETER, type, EPS-3T and a jacketed cell of length 4 or 1 cm attached to a constant-temperature bath (±0.1°C) were employed.

CA is known to ordinarily display a strong acceptor property with some organic donor. THF solutions, containing conjugated polyene (i.e., EA, AO, and VA) and CA, showed 'new' absorption bands in the visible region (Table I), which can be attributed to intermolecular (i.e., CT) interaction. However, the absorbance (d) at the CT-band in all systems decreased with the lapse of time, and finally the characteristic color disappeared at room temperature. It was deduced from NMR measurement that the polyenes reacted with CA under these conditions. That is, a few minutes after preparation, equimolar solutions of donors and acceptor in deuterochloroform, begin to show new NMR signals. Therefore, CT-absorption measurement was tried at low temperature ($-20\sim-70^\circ C$) in order to retard the reaction. Consequently, the absorbance did not vary in regard to time and had reversity at low temperature.

In order to investigate the molar ratio of donor and acceptor in CT-complexes, a continuous variation method was used for the systems EA/CA, AO/CA, and VA/CA in THF. A series of solutions were made, containing different ratios of donor and acceptor, while the total concentration was kept constant at 0.107 M for the system EA/CA, 0.040 M for the system AO/CA, and 0.050 M for the system VA/CA. EA/CA complex was measured at $-20^\circ C$, AO/CA at $-40^\circ C$, and VA/CA at $-40^\circ C$. The plotting of the absorbance at CT-band versus the ratio of donor and acceptor produces a maximum absorbance at a 1:1 ratio (Figure I). Therefore, the molar ratio of donor and acceptor in the complexes is 1:1. No complications arise in the individual absorption of donor and acceptor, because the absorption of either is negligible at the wavelength studied.

For these complexes, the equilibrium constant (K) and the molar extinction coefficient (ε) at CT-band were determined with the method of Benesi and Hildebrand[4)], since the molar ratio of donor and acceptor in these complexes is 1:1.

$$A_O/d = (1/K\varepsilon D_O) + (1/\varepsilon)$$

A series of solution was made with the constant concentration of acceptor (CA) (0.015 M) and the concentrations of donor varying from 0.2 to 0.6 M. EA/CA was measured at -20, -30, $-40^\circ C$, AO/CA at -46, -56, $-66^\circ C$, and VA/CA at -40, -50, $-60^\circ C$. Reasonable linear plots of A_O/d against $1/D_O$ were obtained for these complexes at each temperature (Figure II). Epsilon was calculated from the intercept and K from the slope.

The free energy for the formation of CT-complex[5.a)] (ΔG^0)*, as well as the heat of the formation[5.b)] (enthalpy, ΔH^0), and the entropy[5.b)] (ΔS^0) were determined as well. The results are compiled in Table I.

Each equilibrium constant is considerably smaller in comparison with aromatic CT-complexes[6)]. This may be caused by the fact that the ionization potential of the conjugated polyene[6)] is larger than aromatic donor and the conjugated polyene has less planarity than aromatic donor. Moreover, it is considered from Table I that the interactions between the donor and the acceptor

Figure I. Continuous variation method. Solvent: THF, CA+EA=0.107 mol/l(temp. -20°C), CA+AO=0.040 mol/l(temp.-40°C), CA+VA=0.050 mol/l(temp.-40°C).

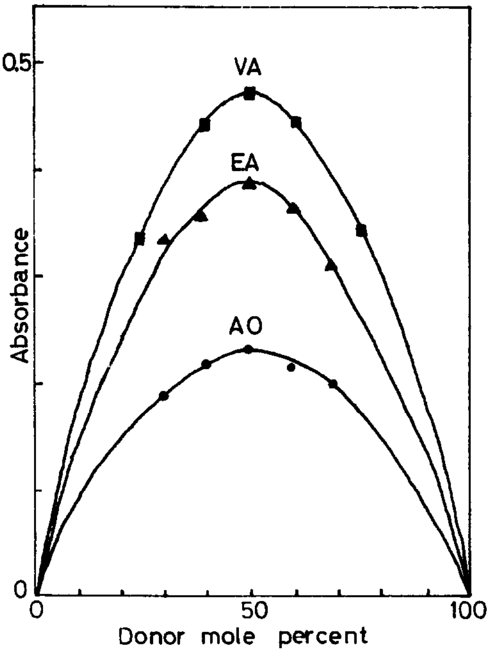
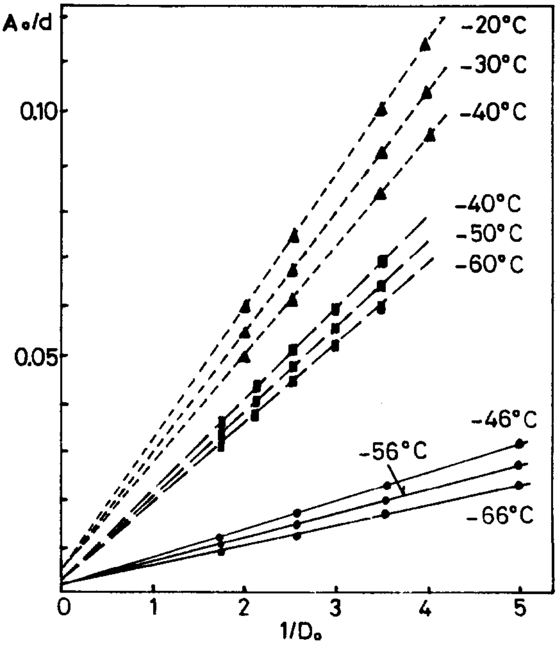


Figure II. Plots of A_O/d against $1/D_O$. Solvent: THF, ----- EA+CA, ——— AO+CA, — — VA+CA.



---

* $\Delta G^0 = -RT(\ln K_C - \ln V_S)$: K_C; equilibrium constant (mol/l), V_S; molar volume

are weaker than that of aromatic CT-complex7), as ΔH^0 and ΔS^0 are very small. The negative entropies are consistent observations, since the formation of CT-complex is the reaction which decreases the disorder of the system.

Table I. Spectral data and thermodynamic constants.

Donor	Acceptor	λ_{max}^{THF} (nm)	ε	temp. (°C)	K (l/mol)	ΔG^0 (Kcal/mol)	ΔH^0 (Kcal/mol)	ΔS^0 (cal/mol deg.)
EA	CA	540	180	-20	0.19	-0.47	-0.85	-1.5
				-30	0.21	-0.49		
				-40	0.22	-0.51		
AO		595	1000	-46	0.19	-0.42	-1.44	-4.4
				-56	0.22	-0.48		
				-66	0.25	-0.51		
VA		640	400	-40	0.13	-0.26	-0.37	-1.6
				-50	0.14	-0.27		
				-60	0.14	-0.29		

References

1). For example, S.Winstein and H.J.Lucas, J.Am.Chem.Soc., 60, 836(1938).

2). F.Ulrike Lichti and J.A.Lucy, Biochem.J., 112, 221(1969).

3). J.W.Verhoeven, I.P.Dirkx, and Th.J.de Boer, Tetrahedron, 25, 3395(1969).

4). R.Foster, Organic Charge Transfer Complexes, p. 129. Academic Press, London

5). a. D.H.Everett, An Introduction to the Study of Chemical Thermodynamics, Chapter 7, Longmans (1959).

b. L.J.Andrews and R.M.Keefer, Molecular Complexes in Organic Chemistry, p. 101. Holden-Day, Inc., San Francisco (1964).

6). L.J.Andrews and R.M.Keefer, Molecular Complexes in Organic Chemistry, p. 26

7). L.J.Andrews and R.M.Keefer, ibid., p. 103.