Charge-transfer complexes of some linear conjugated polyenes

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On adsorption of some electron-acceptor molecules on the solid films of all-*trans*- β -carotene, β -apo-8'-carotenal, astacene and methylbixin a new absorption band appears on the longer-wavelength side of the spectrum in addition to the original bands. The position of this new band is dependent on the electron affinity (E_A) of the acceptor molecules, and the intensity of this band increases with the amount of adsorbed acceptor molecules. A linear relationship between the $\nu_{\max}$ of the new band and E_A was observed. The value of the ionization potential of the polyenes estimated from such linear relationship agrees satisfactorily with the value obtained by other methods. It has been concluded that the polyenes behave as electron donor and first form molecular charge-transfer complexes (of type [polyene·I₂] with iodine) with electron acceptors, these finally dissociating to yield ionic complexes (of type [polyene·I⁺] with iodine).

The charge-transfer complexes are thought (Mulliken, 1952; Szent-Györgyi, 1960) to play an important role in biological systems. The presence of carotenoids (polyenes) in living systems and in plants is well recognized. Some carotenoid pigments are present in cone layers of eyes (Popper & Greenberg, 1941), in olfactory areas (Milas *et al.*, 1939; Briggs & Duncan, 1961; Moulton, 1962), in skin and in membranes (Edwards *et al.*, 1951; Flesch *et al.*, 1955) of animals. Indeed, the presence of carotenoids in chloroplasts strongly suggests their involvement in photosynthesis. It was Platt (1959) who suggested that donor–carotene–acceptor trimolecular complex could be involved in the primary photosynthesis process. Such a complex would shift the carotene absorption band to a much longer wavelength below the absorption bands of chlorophylls, and such a complex would be the energy sink of the whole system. Simple bimolecular charge-transfer complexes may also work in the same way. Charge-transfer mechanisms involving the polyenes may also be responsible for the biological activities associated with these polyenes.

Usually the charge-transfer bands are studied in solutions. Lupinski (1963) observed a new absorption band at 1000 nm (10000 cm⁻¹) in a mixture of β -carotene and iodine in 1,2-dichloroethane solution and attributed this to a charge-transfer band of

β -carotene·I⁺ complex. Ebrey (1967), on the other hand, argued that the band observed by Lupinski (1963), instead of being a charge-transfer band of donor–acceptor type, was a band of β -carotene shifted to a longer wavelength as the consequence of a charge-transfer effect. He suggested that β -carotene·I⁺ complex has several resonance structures for the β -carotene ground state that would equalize bond length and cause the shifting to longer wavelength. The usual method of observing charge-transfer bands in solutions with suitable acceptors has not been successful with the polyenes except with vitamin A (Lucy, 1965, 1969; Lichti & Lucy, 1967, 1969; Lucy & Lichti, 1969).

The important property of the charge-transfer-complex forces is that they are relatively long-range as compared with chemical forces. Before a charge-transfer interaction can take place, the donor and the acceptor molecule or parts of the molecules must be in sufficient proximity to each other. In solution, Brownian motion decreases the possibility of their close approach. In a rigid matrix, the molecules are held in such close proximity that charge transfers are generally facilitated. Thus molecules that seem not to interact in solution may do so in the solid state. To study the charge-transfer complexes of polyenes in the solid state, we have allowed the vapours of some acceptors to be adsorbed on solid films of some polyenes and have collected the spectroscopic data to test whether charge-transfer complexes are really formed in the solid state. The present paper gives the results of this investigation.

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Experimental

The polyenes used in the present investigation were all-*trans*- β -carotene, β -apo-8'-carotenal, astacene and methylbixin. These were obtained from Hoffman-La Roche Co., Basel, Switzerland. We used these chemicals without further purification. Thin films of polycrystals of these polyenes were made on the quartz surface by gently rubbing the material on it. The solid films thus made were exposed to vapours of HNO_3 , I_2 , Br_2 and ICl . These chemicals were of high quality. The absorption spectra at room temperature (28°C) were recorded immediately after exposure of the solid films to vapours. A Spectromom-202 spectrophotometer (Hungarian Optical Works, Budapest, Hungary) was used.

Results and discussion

The room-temperature (28°C) absorption spectrum of all-*trans*- β -carotene in the solid state and the spectra after adsorption of different acceptor vapours are shown in Fig. 1. It is seen that, on adsorption of acceptor vapours, in addition to the original bands of β -carotene, a new band appears on the longer-wavelength side of the spectrum. The

Fig. 1. Electronic absorption spectra of all-*trans*- β -carotene solid film at 28°C after adsorption of different electron-acceptor vapours

For experimental details see the text. Key: curve 1, solid-film spectrum without vapour adsorption; curve 2, HNO_3 -vapour adsorption; curve 3, I_2 -vapour adsorption; curve 4, Br_2 -vapour adsorption; curve 5, ICl -vapour adsorption. The positions, ν_{max} , of the new bands are indicated by vertical marks. Spectra on adsorption of different vapours are not normalized.

observed band with λ_{max} at about 865 nm ($11\,560\text{cm}^{-1}$) in the case of I_2 , we believe, is different from that reported by Lupinski (1963) with λ_{max} at 1000 nm ($10\,000\text{cm}^{-1}$) in β -carotene-iodine in 1,2-dichloroethane solution. Indeed, the charge-transfer band observed in the solid state is usually at longer wavelength than that observed in solution (Matsuo, 1965). Also, the half-width of the band we have observed is approx. 3000cm^{-1} , larger than that of the band observed by Lupinski (1963). In the other polyenes studied a similar new band is observed on adsorption of the acceptor vapours. In Fig. 2 we present the absorption spectra of the polyenes on adsorption of I_2 vapour. The position of this new band depends on the polyene. On adsorption of other acceptor vapours also a similar band appears. We have further examined the effect of the amount of acceptor molecules adsorbed on the donor film surface for all pairs of donor acceptor. This was done by exposing the polyene film to the acceptor vapour for different lengths of time. The maximum length of time of exposure was kept below the time required to reach adsorption saturation under the experimental condition. The actual amount of acceptor vapour adsorbed could not be determined in such experiments. However, the increment of the amount of vapour adsorbed with time in polyene films has been established by adsorption-kinetics studies (Mallik *et al.*, 1979). A typical result is shown in Fig. 3. The intensity of the new band increases with increasing amount of acceptor vapour adsorbed: this is a usual observation for charge-transfer bands. The position of the new band in each

Fig. 2. Electronic absorption spectra of some polyene solid films at 28°C after adsorption of I_2 vapour

For experimental details see the text. Key: curve 1, all-*trans*- β -carotene; curve 2, β -apo-8'-carotenal; curve 3, astacene; curve 4, methylbixin.

polyene is found to be dependent on the acceptor vapours used. Though I_2 , Br_2 and ICl are acceptors of similar nature with electron affinity values close together, the position of the new band in each polyene shows a distinct red-shift with the increasing electron affinity of the acceptor molecules. Only acceptors fairly volatile at ordinary temperature are suitable for such an experiment. As the number of such acceptors is very limited, only a few acceptors could be used. The positions of the new band in different polyenes appearing on adsorption

of various acceptor vapours are summarized in Table 1.

According to Mulliken's theory for formation of a charge-transfer complex, to a first approximation one can relate the energy of the charge-transfer band with the ionization potential of the donor and the electron affinity of the acceptor molecule by the linear relation (Chen & Wentworth, 1975):

$$h\nu_{CT} = I_D^v - E_A^v + C_1 \quad (1)$$

where $h\nu_{CT}$ is the energy of the lowest-energy intermolecular charge-transfer band, I_D^v is the vertical ionization potential of the donor, E_A^v is the vertical electron affinity of the acceptor and C_1 is a constant. Unfortunately, reliable values of vertical electron affinities are very scarce. Apart from the necessary distinction between the vertical and adiabatic or absolute values, different experimental methods yield different results, and also sometimes the substance of interest has not been studied at all. The value of E_A^v for HNO_3 is not available in the literature. Chen & Wentworth (1975) have emphasized that the correlation of $h\nu_{CT}$ with the absolute electron affinities (E_A) of acceptors is consistent with the usual linear equations and their associated assumptions. The adiabatic electron affinities of I_2 , Br_2 and ICl estimated theoretically by Person (1963) were 2.4 ± 0.3 , 2.6 ± 0.3 , and 2.7 ± 0.3 eV respectively, agreeing satisfactorily with the experimental absolute values measured by Hughes *et al.* (1973). We have therefore used these adiabatic electron affinity values as the absolute values. The value of E_A for HNO_3 was taken from Chen & Wentworth (1975).

A plot of $\nu_{max.}$ of the new band of all-*trans*- β -carotene against E_A is shown in Fig. 4. A satisfactory straight line is obtained. The ionization potential of β -carotene can be estimated from this $\nu_{max.}$ -versus- E_A plot. The intercept of this curve gives $I_D + C_1 = 2.44$ eV. In typical donor-acceptor charge-transfer complexes, $-C_1$ is usually about 3 eV (Chen & Wentworth, 1975; Farragher & Page, 1967). This gives a value of the ionization potential of β -carotene as 5.44 eV. The experimental value (Vilesov, 1960; Vilesov & Terenin, 1960) of the

Fig. 3. Enhancement of the intensity of the new band with the amount of adsorbed acceptor molecules on the solid film of β -apo-8'-carotenal at 28°C

For experimental details see the text. The continuous line is for the neat solid-film spectrum. The broken lines represent the spectra after I_2 -vapour adsorption: curves 1-4 in order of increasing amount of I_2 molecules.

Table 1. Position ($\nu_{max.}$) of the new band appearing on adsorption of different acceptor vapours on the solid films of some polyenes

For experimental details see the text.

Acceptor used	E_A (eV)	$\nu_{max.}$ (cm^{-1}) for			
		all- <i>trans</i> - β -Carotene	β -Apo-8'-carotenal	Astacene	Methylbixin
HNO_3	1.83	13 900	—	—	—
I_2	2.40	11 550	12 000	13 150	13 200
Br_2	2.60	11 300	11 800	12 800	13 000
ICl	2.70	11 100	11 500	12 500	12 700

Fig. 4. Plot of $\nu_{\max.}$ against E_A for all-trans- β -carotene. For details see the text.

Fig. 5. Plot of ν_{CT} against I_D for charge-transfer complexes of a number of donors with I_2 acceptor. For details see the text. The donors are: 1, benzene; 2, toluene; 3, *m*-xylene; 4, mesitylene; 5, naphthalene; 6, durene; 7, pentamethylbenzene; 8, triphenylene; 9, hexamethylbenzene; 10, chrysene; 11, anthracene; 12, pyrene. The values of ν_{CT} and I_D have been taken from Foster (1969) and Chen & Wentworth (1975) respectively.

ionization potential (measured from photoemission thresholds) of β -carotene is 5.5 eV. This agreement supports the validity of the above linear plot and also of the charge-transfer concept for this complex. From eqn. (1) one expects a slope of unity for the $h\nu_{CT}$ -versus- $E_A^\vee$ plot. Fig. 4 gives a slope of 0.44. This low value for the slope could be due to the electron-affinity values used for the plot being absolute rather than vertical. Further, eqn. (1) is only an approximate one. Indeed, such a deviation of slope from unity is a general observation in these types of experiments (McConnel *et al.*, 1953; Foster, 1960).

The use of charge-transfer spectra for the evaluation of a ionization potentials is well known. The ionization potential of an unknown donor can be obtained from the ν_{CT} -versus- I_D plot for a large number of other donors with a common acceptor,

provided that the value of ν_{CT} for this unknown donor is known for the same acceptor. We have made the ν_{CT} -versus- I_D plot for a large number of other donors with I_2 acceptor as shown in Fig. 5 from the values reported in the literature (Foster, 1969), and have evaluated the value of I_D for all-trans- β -carotene from this plot. This value 5.56 eV is in good agreement with the experimental value and the value obtained from the ν_{CT} -versus- $E_A^\vee$ plot. The ν_{CT} values for the aromatic donors in the plot of Fig. 5 are for the complexes in solutions, whereas the value of $\nu_{\max.}$ for this polyene complex is for the solid state. However, the consequent uncertainty in this evaluated I_D value of the polyene may be of the order of 0.1 eV for the maximum. Though the number of electron acceptors examined for this investigation is small, this agreement in the value of ionization potential adds further credence to the above charge-transfer concept for the complex.

The relationship between the ionization potentials of two donors and the values of $\nu_{\max.}$ corresponding to their charge-transfer complexes with a common acceptor, assuming that the C_1 values do not differ much in the two complexes, can be written as (from eqn. 1):

$$I_D(\text{donor-2}) = I_D(\text{donor-1}) + h\nu_{CT}(2) - h\nu_{CT}(1) \quad (2)$$

From this eqn. (2) one can estimate the value of ionization potential of donor-2 if the ionization potential of the donor-1 and the associated values of the ν_{CT} are known. We have estimated the values of the ionization potentials of β -apo-8'-carotenal, astacene and methylbixin from this eqn. (2) by assuming I_D (donor-1) to be 5.50 eV (experimental value) for β -carotene and taking $\nu_{\max.}$ of the new band for I_2 -vapour adsorption in all these polyenes. The estimated values are 5.56, 5.69 and 5.70 eV for β -apo-8'-carotenal, astacene and methylbixin respectively. Unfortunately, the values of ionization potential of these polyenes have not been reported.

The room-temperature absorption spectrum of astacene after adsorption of I_2 vapour is shown in Fig. 6. From this spectrum it is observed that, in addition to the new band in the longer-wavelength side, another new absorption band is also observed at about 366 nm (27300 cm^{-1}). This is the well-known absorption band of the I_3^- ion (Slifkin, 1971). The other absorption band of this molecular ion, expected at about 295 nm (33900 cm^{-1}), has possibly been merged with the original band of this polyene in this region. This band of the I_3^- ion is also observed with the other polyenes under study. Considering the experimental technique of adsorbing the acceptor molecules on the polyene films, we believe that the possibility of formation of I_3^- ion in enough concentration as a consequence of the presence of a trace of water is rather remote. It

Fig. 6. Electronic absorption spectra of astacene solid film at 28°C

For experimental details see the text. The continuous line is for the neat solid-film spectrum and the broken line for the spectrum after I_2 -vapour adsorption. The positions of the new bands are indicated by vertical arrows.

Fig. 7. Change in intensity with time of the new band (11550 cm^{-1}) for I_2 -vapour adsorption on all-trans- β -carotene film

For experimental details see the text.

therefore seems that the results reported in Fig. 4, where the E_A values are of acceptor molecules, and the observation of the I_3^- ion band suggest that, with I_2 , possibly through the reaction

the polyenes form charge-transfer complexes with iodine. The new band arises as a result of the formation of the $[\text{polyene} \cdot I_2]$ complex. The I^- ion finally could combine with free iodine to give I_3^- . It is therefore expected that the $[\text{polyene} \cdot I_2]$ complex will dissociate with time. In Fig. 7 we show that the intensity of the new band with $\lambda_{\text{max.}} = 865\text{ nm}$ (11560 cm^{-1}) indeed decreases with time, suggesting such a dissociation. The band reported by Lupinski (1963) in a mixture of β -carotene and I_2 in solution at 1000 nm (10000 cm^{-1}) and discussed by Ebrey (1967) is in all likelihood the band of the $[\beta\text{-carotene} \cdot I^+]$ complex.

The interactions between the polyenes and I_2 that we have studied have some resemblance to those between retinol and I_2 reported by Lucy & Lichti (1969). They reported that under suitable conditions retinol and I_2 first form a blue $[\text{retinol} \cdot I_2]$ complex absorbing at 670 nm (14925 cm^{-1}), this subsequently dissociating to yield an ionic complex of the type $[\text{retinol} \cdot I]^+ I^-$ in which the $[\text{retinol} \cdot I]^+$ complex absorbs at 870 nm (11494 cm^{-1}). Unfortunately, the limitation of the sensitivity of the detector in our experimental set-up did not permit us acquisition of reliable results beyond 1000 nm , where, according to Ebrey (1967), the $[\text{polyene} \cdot I^+]$

complexes are expected to absorb, i.e. where the corresponding polymethines would absorb. Assignment of the observed new bands to molecular $[\text{polyene} \cdot \text{acceptor molecule}]$ complexes is based on the fact that the $\lambda_{\text{max.}}$ of these bands depends strongly on the properties of the acceptor molecule, contrary to that expected for inner $[\text{polyene} \cdot I^+]$ complexes. The $\lambda_{\text{max.}}$ of the observed bands of various polyenes with a particular acceptor is also at much higher energy than that where the corresponding polymethine absorbs.

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