

Photoconductive properties of zeaxanthin in a sandwich cell

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Abstract. Photoconduction decay in zeaxanthin in a sandwich cell has been measured as a function of applied field and temperature in longer time domains (5–35 s). The results show that the gap states decrease exponentially with characteristic temperature $T_c \approx 450$ K at an applied field of 1.77×10^3 V/cm. When the sample temperature is 293 K, T_c is found to be voltage-dependent and follows the empirical relation $T_c \approx A \exp(-bV)$. The field effect on T_c is suggested to arise from the field effect on trapping rate. Light intensity dependence of photocurrent satisfies the power law $I_{ph} \propto I_b^\gamma$ with γ varying between 0.61 and 0.58 depending on the applied voltage at low excitation light intensity. At high intensities $\gamma = 1.2$. T_c values evaluated from decay and light intensity dependence measurements show excellent correlation.

Keywords. Organic photoconductors; zeaxanthin; photoconductivity decay; exponential trap distribution; field dependence; temperature dependence.

1. Introduction

In continuation of our programme to study the photoconductive properties of polyenes (Ghosh *et al* 1986; Pal *et al* 1987, 1988), we have now extended our investigations to zeaxanthin, a long chain conjugated polyene (figure 1). Like other carotenoids, zeaxanthin is also known to be present in the photosynthetic units of plants and in green and purple bacteria and is likely to be involved in photosynthesis (Rosenberg 1961, 1966; Falk and Fatt 1966; Cherry and Chapmann 1967; Hoshino and Tateishi 1976; Goodwin 1980). Photocarrier generation and recombination processes in this material are therefore, of considerable interest.

Decay kinetics of organic photoconductors provide a useful tool for obtaining

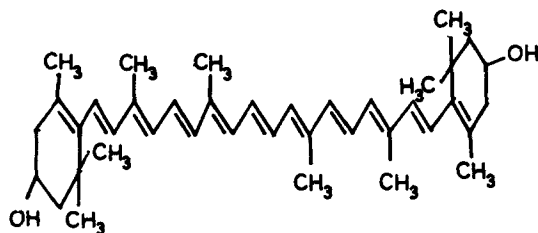


Figure 1. Molecular structure of zeaxanthin.

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information about the distribution of traps in the material. Traps which have been filled during the excitation of the material will empty, when excitation is removed, at a rate depending on their capture cross-section and ionization energy. If it is assumed that retrapping of carriers freed from traps is negligible, then an exponential decay is expected. If many different types of traps are present with different capture cross-sections and ionization energies, the decay curves follow a time-dependence which can be expressed generally as,

$$I_{ph} \propto t^{-n}, \quad (1)$$

where n may also vary in different ranges of t (Huang *et al* 1983). The photocurrent during decay will be proportional to the rate at which carriers are thermally freed from traps, multiplied by the appropriate life-time for the freed carriers. The energy spectrum of the gap-distribution can be obtained from a study of time- and temperature-dependence of photocurrent. Another interesting method for obtaining information about the gap states is from the study of the intensity-dependence of steady-state photoconductivity. We have used the decay in the long-time domain and the light intensity-dependence of steady-state photocurrent to get information about the distribution of gap states in zeaxanthin in a sandwich cell. In this paper we report the results of our investigation.

2. Experimental

High quality zeaxanthin used in this investigation was obtained as a gift from the Hoffmann-La Roche Co., Switzerland. The purity of the sample was checked by taking the absorption spectra and was used without further purification. The powdered sample was used in a sandwich cell with stainless steel and tin oxide-coated glass electrode. The cell was placed in a suitably designed conductivity chamber (Mallik *et al* 1979) with a quartz window through which light can pass and illuminate the sample. For current measurements Keithley's programmable electrometer model 617 was utilised. The electrometer has a built-in isolated d.c. voltage supply which can be adjusted between -100 V and $+100$ V. Voltages upto $+100$ V were applied across the electrodes from this source and for higher voltages, a high voltage regulated power supply (model 7333 APLAB, India) was used. The electrometer has an internal data storage facility as well where data can be stored at a preprogrammed time interval which can be recalled later. This data storage facility was utilised in recording photoconductivity decay with time. Temperature measurements were made by a copper-constantan thermocouple and a panel meter (HIL 2301, India). A 100-watt xenon lamp was used to illuminate the sample and a mechanical shutter was used for photoconductivity decay measurements. Various neutral density filters were interposed in the beam path to control the light intensity. A Shimadzu spectrophotometer (model no. 210A) was used to run the absorption spectrum. The sandwich cell thickness and area were maintained at 0.0025 cm and 0.25 cm² respectively. After each voltage application sufficient time was allowed for the attainment of equilibrium current value. Several measurements were made in order to ensure reproducibility of results both in vacuum and in an atmosphere of dry nitrogen.

3. Results and discussion

The decay kinetics of zeaxanthin studied at different applied fields and temperatures in the long time domain are shown in figures 2 and 3, respectively. Though these decay curves show the decay of the photocurrent, the dark current component is contained in the measured values. This is reflected in the magnitude of current rise with temperature in figure 3. Our measured thermal activation energy of the dark current is 2.18 eV and that of the photocurrent is 0.275 eV. The double logarithmic plots of photocurrent vs. time at different voltages and temperatures are found to be linear indicating a power-law dependence of the photocurrent on time. Assuming an exponential distribution of localized states the power law dependence of photocurrent on time is given by (Tiedge *et al* 1981; Huang *et al* 1983),

$$I_{ph} \propto t^{-(1-T/T_c)} \quad (2)$$

where T_c is a characteristic constant for exponential trap distribution and is a measure of the rate at which trap density falls with energy.

A physical picture leading to time resolution is very simple. As soon as we switch off the light, the majority of the photogenerated carriers recombine either directly or through dominating trapping levels. This is achieved in a very short time. The remaining carriers can be considered as forming a carrier packet which can now be employed to probe various levels of the trap distribution at various trap depths at different times. Let the carrier packet probe the localised state at an energy E_d from the mobility edge E_c at a time t , then

$$E_c - E_d = kT \ln(v_0 t), \quad (3)$$

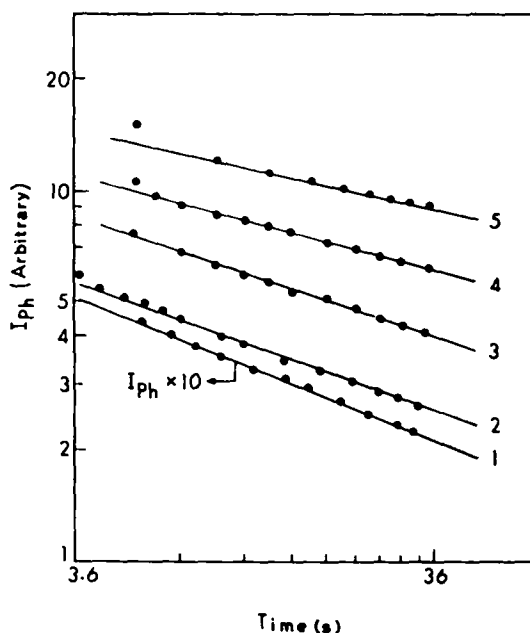


Figure 2. Dependence of photocurrent on time at constant temperature 293 K for different applied voltages (1) 5, (2) 40, (3) 60, (4) 80 and (5) 100 V.

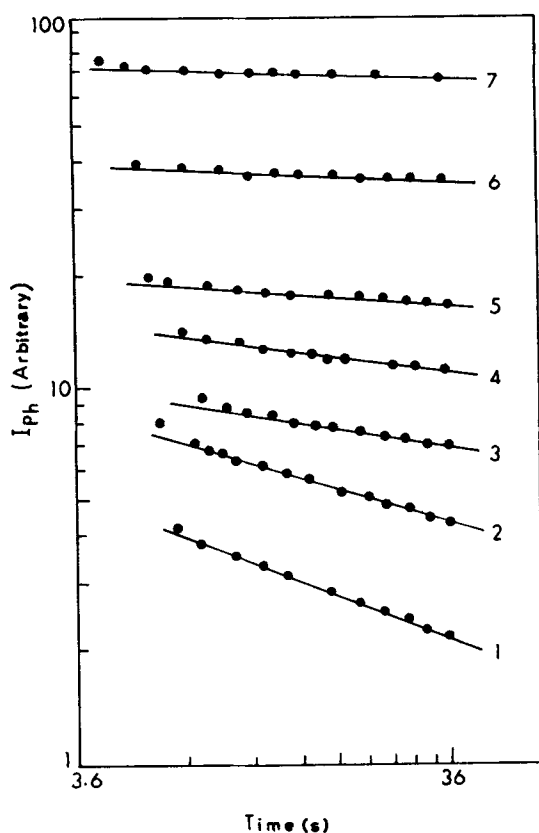


Figure 3. Dependence of photocurrent on time at constant applied voltage 5 V at different temperatures (1) 293, (2) 298, (3) 300.5 (4) 303, (5) 305.5, (6) 309 and (7) 313 K.

where k is Boltzmann constant and ν_0 has a value of $2.2 \times 10^{11} \text{ s}^{-1}$ for polyvinyl carbazole estimated from x-ray induced current measurement in a nanosecond time domain (Hirsch 1979). Using (3) it is possible to convert a time scale into an energy scale. It can be estimated that after one second the carrier packet will be probing the level at a depth of 0.70 eV from the conduction band E_c .

By using (2) T_c can be calculated from the slope of $\log I_{ph}$ vs. $\log t$ plots at different voltages and temperatures. The value of T_c seems to be constant for a particular voltage and temperature. This indicates that the rate of decline of trap density with increasing time or increasing energy depth in the time domain of our studies is almost constant.

We have also studied the field dependence and temperature dependence of the decay kinetics. It is observed that T_c decreases with increase in voltage which is similar to that observed in methylbixin (Pal *et al* 1987). In figure 4 we have shown the plot of $\ln T_c$ vs. V for a constant T which is a straight line with negative slope. So we can express the voltage dependence of T_c as

$$T_c \approx A \exp(-bV), \quad (4)$$

where A and b are constants. Field effects on T_c may arise from a field effect on

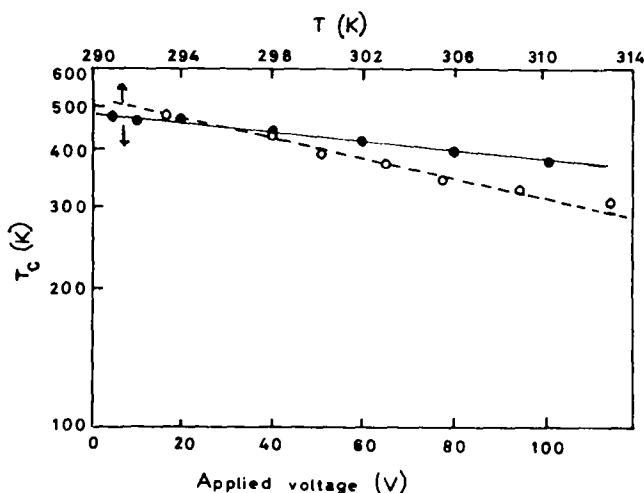


Figure 4. Dependence of T_c on applied voltage of constant temperature 293 K (●) and on temperature at constant applied voltage 5 V (○). Arrows indicate the relevant scales.

trapping rate. Field-dependent trapping time in organic charge transfer salts, polymers and polyenes have been reported (Pal *et al* 1987; Harrer and Mohwald 1975; Seiferheld *et al* 1983).

Similarly, T_c is found to decrease with the increase in temperature. From (3) again we can say that we can probe deeper traps at higher temperatures for the same values of t and applied voltage. So we can conclude that the rate of decline in trap density decreases as we go deeper below the conduction band. Similar temperature-dependence of T_c has also been reported (Orenstein and Kastener 1981).

We have also studied the excitation light intensity dependence of the photocurrent at different applied voltages. The sample in a sandwich cell was irradiated through the semitransparent SnO_2 electrode which was made positive. It is observed that for all the applied voltages and over the entire range of intensity we worked with, the photocurrent I_{ph} is related with the excitation light intensity I_B through the power law,

$$I_{ph} \propto I_B^\gamma. \quad (5)$$

The $\log I_{ph}$ vs. $\log I_B$ plot is shown in figure 5. For all the applied voltages, the plots are sublinear at low excitation light intensities but at high intensities each of them changes to superlinearity.

In the sublinear region γ values lie in the interval $0.5 < \gamma < 1$. Such sublinear intensity dependence of steady-state photoconductivity can be explained by the cooperation of recombination centres and exponentially distributed traps (Rose 1963; Stockmann 1969; Meier 1974). The decrease in the value of sublinear γ with the increase in the electric field suggests that there is at least one kinetically important process which is field dependent. This may be field dependent rate of detrapping or rate of recombination.

The superlinear dependence of steady state photocurrent on excitation light intensity has been explained by Rose (1963) to be due to the presence of two types of recombination centres in the trap distribution, one type having larger capture cross-section for the majority carriers and the other type having larger capture cross-section

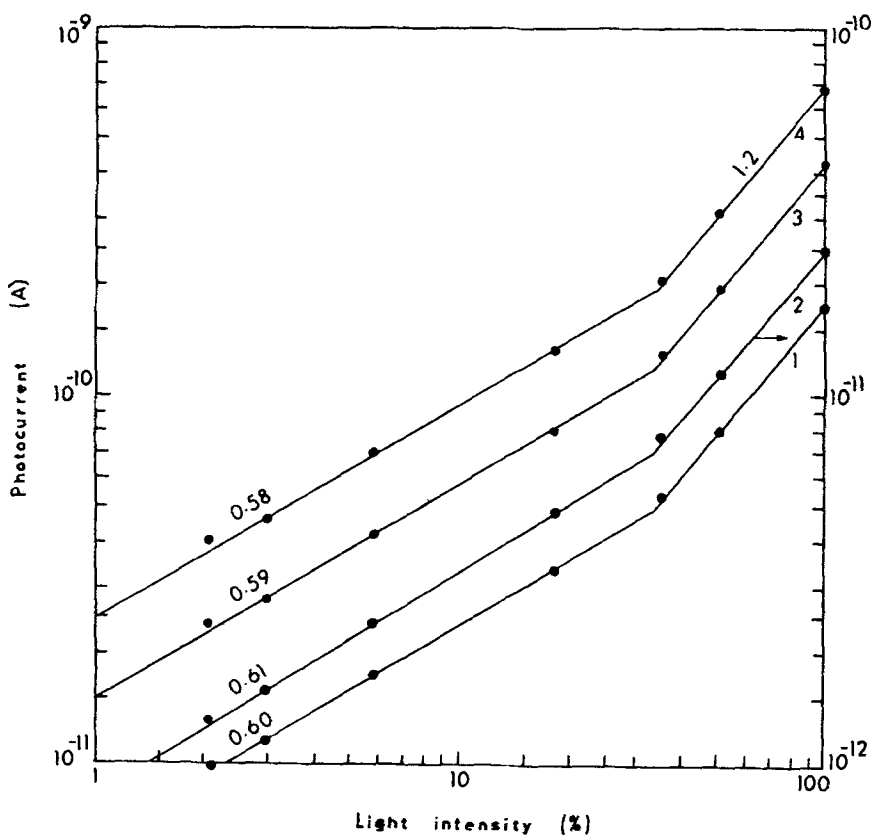


Figure 5. Light intensity dependence of photocurrent on a logarithmic scale at different applied voltages (1) 20, (2) 5, (3) 40 and (4) 60; γ values are shown.

for the minority carriers. At low light intensity, if the minority carrier-capturing centres lie outside or partially outside the two quasi-Fermi levels, photosensitivity is determined only by the majority carrier capturing centres and sublinear $\log I_{ph}$ vs. $\log I_B$ plots are obtained, as discussed earlier. When light intensity is increased, the quasi-Fermi levels move toward the respective band edges embracing more and more minority carrier-capturing centres and superlinear-dependence of steady state photoconductivity on excitation light intensity is obtained.

However, we have performed all our decay measurements with a fixed excitation light intensity which lies in the sublinear region and henceforth we will discuss γ and the corresponding T_c in the sublinear region only.

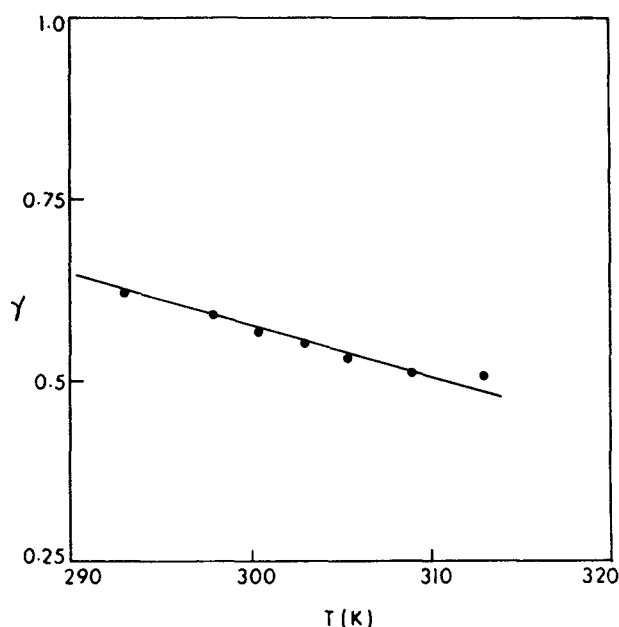
Again, by using the model of Rose (1963) γ in (5) can be related to T_c in (2) by the relation,

$$T_c = (\gamma T)/(1 - \gamma). \quad (6)$$

Thus, we can calculate the values of T_c for different applied voltages by using the corresponding experimental values of γ . These evaluated T_c values are in good agreement with the experimental T_c values obtained from $\log I_{ph}$ vs. $\log t$ plots at different applied voltages. T_c values obtained by these two methods are listed in table 1 for easy comparison.

Table 1. Voltage dependence of T_c .

Applied voltage (V)	Value of T_c (K) from $\log I_{ph}$ vs. $\log t$ plot at 293 K	Calculated value of T_c (K) from (6) at 293 K
5	473	459
10	465	—
20	460	440
40	445	422
60	432	405
80	397	—
100	377	—

**Figure 6.** Temperature dependence of γ evaluated from the photoconductivity decay measurements at different temperatures at constant applied voltage (5 V).

From experimental values of T_c at different temperatures we can calculate the corresponding γ values using (6). We can see that γ values decrease with the increase of temperature and this is shown in figure 6. This observation is similar to that reported by Aoyagi *et al* (1972) for zinc phthalocyanine. However, unlike that in zinc phthalocyanine, in zeaxanthin the $0.5 < \gamma < 1$ condition is satisfied at the working light intensity region indicating that the diffusion effect of charge carriers is negligible. Thus, trapping and recombination of photocarriers in exponential trap distribution, which changes with temperature and with applied field, satisfactorily explains photoconductivity decays in the long-time domain in this polyene material.

The dark activation energy as well as the photoconduction threshold energy of the polyenes is known to depend on the number of conjugated π -electrons (Meier 1974). However, polyenes with identical chain lengths but with different end groups show appreciable variation in their conductive properties. Zeaxanthin is structurally similar

to β -carotene except that the two end rings contain one additional OH group each. Both dark and photoactivation energies are significantly higher in zeaxanthin [$E_d(\beta\text{-carotene}) = 1.52\text{ eV}$, $E_d(\text{zeaxanthin}) = 2.18\text{ eV}$, $E_{ph}(\beta\text{-carotene}) = 0.18\text{ eV}$, $E_{ph}(\text{zeaxanthin}) = 0.275\text{ eV}$].

Zeaxanthin, like other polyenes (Roberts and Schmidlin 1969) shows 'non-extrinsic' behaviour in dark conduction but becomes extrinsic in photoconduction. This extrinsic behaviour may originate from the localized levels formed at the molecular *cis*-bands created by photoisomerization of the molecule.

Conclusions

1. Long time decay measurements of photocurrent in zeaxanthin polycrystals in a sandwich cell show that there is an exponential distribution of trap states in the band gap in this material.
2. The temperature and voltage dependence of long time decay measurements suggest that there is at least one kinetically important process which is both temperature and field dependent; this may be rate of detrapping or rate of recombination.
3. Light intensity dependence of photocurrent suggests that there are two types of recombination centres; one type having larger capture cross-section for the minority carriers and the other type having larger capture cross-section for the majority carriers.

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