Electron-transfer Reactions involving Chlorophyll a and Carotenoids

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Summary Efficient electron-transfer reactions occur between carotenoid and chlorophyll photosynthetic pigments.

The pigment systems involved in photosynthesis are thought to contain several hundred chlorophyll molecules as light harvesters and a small number of special chlorophyll molecules as reaction initiating centres.[1] Thus, photo system 1 (PS1) in green plants is said to contain reactive centres of special chlorophyll molecules called P_{700} (P_{870} in photosynthetic bacteria[2]). The primary reaction of P_{700} is a photoxidation to produce a radical cation of chlorophyll ($\text{chl}^{\cdot+}$).[3] Subsequent processes which regenerate chlorophylll from $\text{chl}^{\cdot+}$ or accept the electron released by the primary reaction are not well understood and thus electron-transfer reactions involving chlorophyll and $\text{chl}^{\cdot+}$ are of considerable interest. Carotenoids such as β-carotene are always associated with chlorophylls in the plant and thus reactions between chlorophylls and carotenoids are of significance in the overall photosynthetic process. We now report two efficient electron-transfer reactions each involving chlorophyll a and a carotenoid.

The reactions we have detected are shown in reactions (1) and (2), where C is the carotenoid, namely all-*trans*

$$\text{C}^{\cdot+} + \text{chl a} \rightarrow \text{C} + \text{chl a}^{\cdot+} \qquad (1)$$

$$\text{C}^{\cdot-} + \text{chl a} \rightarrow \text{C} + \text{chl a}^{\cdot-} \qquad (2)$$

β-carotene or all-*trans* lycopene.

The positive and negative radical ions of the polyenes have recently been reported.[4] In the present work these ions were generated by nanosecond pulse radiolysis (9—12 MeV) of the carotenoids (typically 10^{-4}M—10^{-5}M in hexane), and monitored by their light absorption as a function of time before and after the electron pulse. For β-carotene, the positive and negative ions were monitored at 1050 nm and 880 nm respectively while the monitoring wavelengths for lycopene were 1070 nm and 950 nm, the wavelengths corresponding to the reported[4] maxima in the spectra of the polyene ions.

Chlorophyll a was extracted from spinach by a technique similar to that of Zscheile and Comar,[5] the final purity being confirmed by the ratio of the optical densities of the red and blue absorption peaks.

Table. Second-order rate constants (k) for the reactions between carotenoid ions and chlorophyll a

	$10^{-9}k$ ($\text{M}^{-1}\,\text{s}^{-1}$)	
	β Carotene	Lycopene
Reaction 1 (positive ions)	$6{\cdot}0 \pm 1{\cdot}0$	$1{\cdot}7 \pm 0{\cdot}3$
Reaction 2 (negative ions)	$8{\cdot}5 \pm 1{\cdot}0$	$7{\cdot}0 \pm 1{\cdot}0$

Transients obtained by pulsing chlorophyll a (typically 10^{-4}M) in hexane are composed of three spectrally overlapping species, namely $\text{chl}^{\cdot+}$, $\text{chl}^{\cdot-}$ and the chlorophyll triplet state. To resolve these into individual spectra we used nitrous oxide gassed solutions, methanolic solutions and lifetime considerations. The spectra obtained for $\text{chl}^{\cdot+}$ and $\text{chl}^{\cdot-}$ compare well with those of Seki *et al.*[6] who studied chlorophyll a alone by pulse radiolysis of benzonitrile and tetrahydrofuran solutions.

When either a polyene or chlorophyll a is pulsed alone the decay of both the positive and negative ions is almost totally a second-order process, the corresponding rate constants all being greater than the diffusion allowed value and in the range 1—30 × $10^{11}\text{M}^{-1}\,\text{s}^{-1}$. The fact that these values are above the diffusion controlled rate implies that the major mode of decay in hexane solution is a mutual reaction of the positive and negative ions.

The rate constants of the reactions (1) and (2) for both β-carotene and lycopene were obtained by monitoring the increased rate of decay of the polyene ion (approximately 10^{-8}M, formed by the electron pulse) after adding varying concentrations of chlorophyll a (*ca.* 10^{-4}M). The results obtained are given in the Table.

Both processes occur at near the diffusion limit implying very efficient reactions in which most encounters between carotenoid ion and chlorophyll a result in an electron transfer.

When this work was begun we attempted to observe processes such as the reverse of reaction (1) since we considered that such a route, in which the carotenoid acts as an electron donor, may be open to regenerate chlorophyll from $\text{chl}^{\cdot+}$. However, even with a favourable choice of experimental conditions we could detect no reaction at all between either $\text{chl}^{\cdot+}$ or $\text{chl}^{\cdot-}$ and β-carotene. Thus we conclude that reactions (1) and (2) are in effect one-way processes.

Carotenoids are already thought to act both as accessory pigments in photosynthesis and as protectors for chlorophyll against the damaging effects of singlet oxygen. Our results concerning the detection of two further efficient 'in vitro' reactions between carotenoids and chlorophyll may indicate that carotenoids play other, as yet not understood, roles in the photosynthetic process.

We thank Dr. P. Mathis for discussions, Miss E. H. Reid for technical assistance, and Hoffman La Roche for the donation of the polyenes. This work was supported by grants from the S.R.C., the Cancer Research Campaign, and the M.R.C. J.L. acknowledges a S.R.C. Research Scholarship.

(*Received*, 13*th November* 1975; *Com.* 1268.)

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