$$\frac{k_T}{k_H} = \frac{d(HT)}{d(H_2)} \times \frac{(Ph_3SiH)}{(Ph_3SiT)} = \log \frac{(HT)_\infty - (HT)_2}{(HT)_\infty - (HT)_1} \Big/ \log \frac{(H_2)_\infty - (H_2)_2}{(H_2)_\infty - (H_2)_1}$$

where $(HT)_t$ refers to the amount of tritium and $(H_2)_t$ to the volume of gas collected up to time t. The average value of k_T/k_H, over the course of more than 40% reaction is 0.796 ± 0.004.

This result is in good agreement with a theoretical value of 0.8 calculated[6,7] considering only the stretching frequencies of the Si–H and H–H bonds in the proposed model. The corresponding theoretical value of k_D/k_H is 0.9.

TABLE I

HYDROLYSIS OF TRIPHENYLSILANE-*t*

Fraction	Reaction cumulative %	H_2, mmole	HT, μcuries	HT/H_2, μcuries/mmole	$k_T k_H$
1	16.2	0.286	20.9	73.1	0.803
2	24.8	0.151	11.2	74.2	0.792
3	40.6	0.279	21.5	77.1	0.794
4	100.0	1.046	104.0	99.4	
Total		1.762	157.6	89.4	

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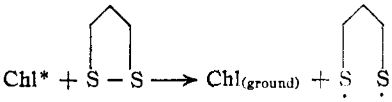
RECEIVED OCTOBER 1, 1952

A POSSIBLE PRIMARY QUANTUM CONVERSION ACT OF PHOTOSYNTHESIS[1,2]

Sir:

To account for the observation[3,4,5] that illumination prevents the appearance of newly assimilated carbon in the compounds of the tricarboxylic acid cycle, it was suggested[5] that the light shifts the steady-state condition of the thioctic acid-containing coenzyme[6,7] (protogen, lipoic acid, thioctic acid, P.O.F.) toward the reduced (dithiol) form, in which condition it is incapable of oxidatively decarboxylating pyruvic acid,[8,9] newly formed from CO_2, to give rise to the acetyl-CoA[10,11,12] required to bring this carbon into the compounds of the Krebs cycle. We are here reporting some observations leading to the further suggestion that this shift toward the dithiol form is the *direct* result of the light action and that a biradical formed by dissociation of the disulfide bond in a strained five-membered disulfide containing ring (as in 6,8-thioctic acid and trimethylenedisulfide) is the species in which the quantum absorbed by the plant pigments and stored as electronic excitation in chlorophyll[13] appears first as chemical bond potential energy; *i.e.*, that a possible primary quantum conversion act of photosynthesis is represented by the equation


(I)

Subsequent abstraction of H atoms[14,15] from a suitable donor by the thiyl free radicals would lead to the dithiol which would be reoxidized ultimately by CO_2. The residual oxidation product of the H donor would lead in the end to molecular oxygen. It is obvious that on both the reductant and oxidant sides the chemical products of the conversion of several quanta will be required to accomplish the reduction of each CO_2 molecule and the generation of each O_2 molecule.

These subsequent reactions, being strictly chemical, may lead to diverse energy rearrangements. For example, the chemical potential of reduced carbon might be converted by oxidative phosphorylation reactions into the energy of phosphoric anhydrides which, in turn, could raise the potential energy of intermediates in the reaction sequences leading to the evolution of molecular oxygen and to the reduction of CO_2.[16,17]

A value of the dissociation energy for this particular disulfide link lying in the region of 30–40 kcal. would constitute not only permissive evidence for reaction (I) but positive evidence in its support, since hitherto it has been difficult to suggest any likely primary chemical step capable of usefully absorbing the greater part of the ≃ 30–40 kcal. quantum of electronic excitation available for photosynthesis. Estimates of D(RS-SR) from simple open chain compounds range from 50[18] to 70[19] kcal. However, the fact that 5,8-thioctic acid is colorless, while 6,8-thioctic acid is yellow,[20] suggested that the incorporation of the S—S bond into a 5-membered ring might indeed introduce sufficient strain into it so as to reduce the S—S dissociation energy by as much as 25–30 kcal., thus bringing it down into the required range. A number of experiments have been performed using the product of the reaction of Na_2S_2 with $(CH_2)_3Br_2$ (trimethylenedisulfide) as a model substance. Its

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[2] J. A. Barltrop, Rockefeller Fellow, 1952–1953, while on leave from Brasenose College and the Dyson Perrins Laboratory, Oxford University, England.

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absorption spectrum together with that of the two thioctic acids and *n*-propyl disulfide is shown in Figure 1. A light-induced fading of diphenylpicrylhydrazyl[22] at room temperature and dependent upon the presence of the disulfide was demonstrated. A photochemical polymerization of the disulfide by light of wave length greater than 4,000 Å. was sensitized by Zn tetraphenylporphin. These results may be taken to indicate that the dissociation energy of the disulfide bond in this compound is something less than 50 kcal. and that this dissociation may be brought about by energy transfer from some other molecule in a suitably excited state.

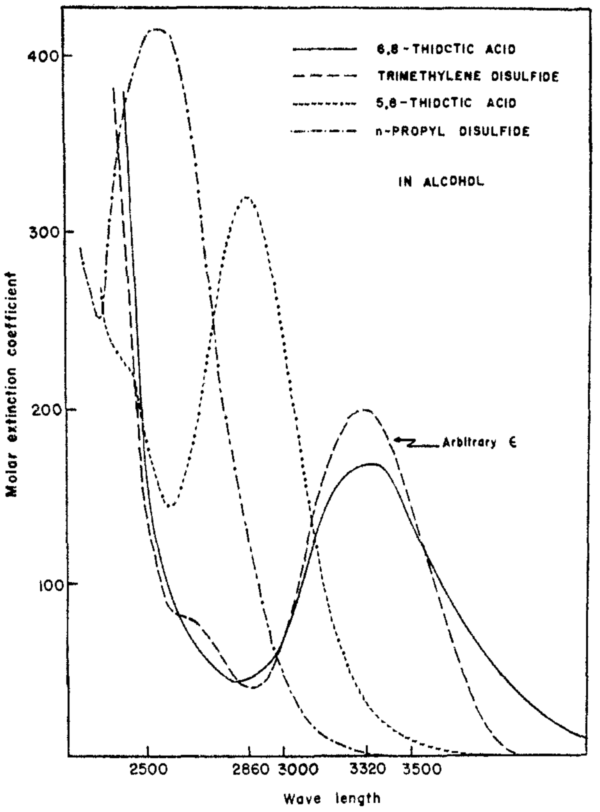

Fig. 1.—Absorption spectra of several disulfides.[33]

That such energy transfers may take place, and especially efficiently in condensed systems, has been amply demonstrated.[23,24,25,26,27] Since the grana have the optical properties of a condensed chlorophyll phase,[28,29,30,31] a quantum absorbed anywhere within that phase is very rapidly transferred among the identical molecules of that phase at the singlet or the triplet levels. Concomitant with this, there occurs a decrease in the probability of emission as fluorescence[23,24,25,32] and hence an increase in the availability of the quantum for chemical transformation (disulfide fission). In such a sytem, the high efficiency of energy conversion may be retained even though the ratio of chlorophyll to disulfide molecules be large (10^2–10^3).

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[33] We are indebted to Mr. Paul Hayes for the determination of these absorption spectra.

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ELECTROCHROMATOGRAPHIC SEPARATIONS OF RARE EARTHS

Sir:

Differential electrical migration in moist filter paper,[1,2,3] which has provided continuous[3] and discontinuous[2] separations of many ions, has now been applied to the separation of rare earths. These applications have incorporated many of the desirable physical and sorptive features of paper chromatography, and they have also utilized the principles of complex formation previously employed for the ion-exchange chromatography of rare earths.[4] They have yielded the resolved ions in a readily detectable and recoverable form.

For one-way, discontinuous migrations, filter paper (Eaton-Dikeman, Grade 301, 0.03 inch thick)[1] 3 to 6 feet by 20 inches was moistened with the electrolytic solution. About 50 μl. of the radioactive mixtures (about 0.3 μc. per component) and separate reference solutions of the components were added near the center.[1] The paper was encased in a polyethylene sheet, and the ends were dipped into separate portions of the electrolytic solution (8 l.) After electrolysis (5 v. per cm.,

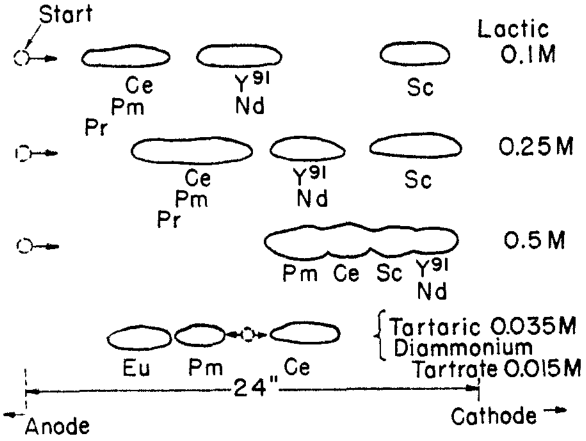

Fig. 1.—Migration of rare earths in lactic acid (24 hr.) and in tartrate solution (48 hr.).

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