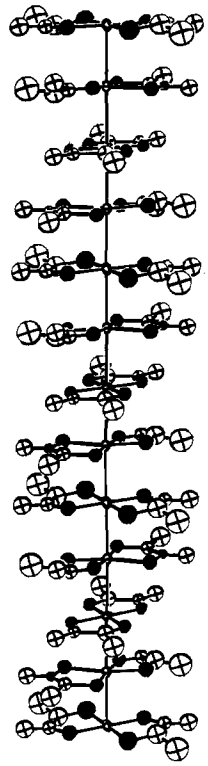

Figure 2. Three wavelengths of the Pt chain along the *c* axis of the unit cell showing the staircase staggering network of oxalate ligands each 45° to the ligand above and below it in the chain. The chelated oxygen atoms are in black.

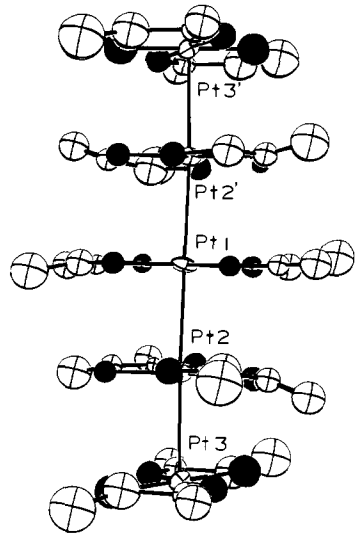

Figure 3. A single wavelength of the Pt chain shows the chain distortion and the ligand nonplanarity. The chelated oxygen atoms are in black.

equivalent Pt atoms in the chain and two Pt–Pt distances, 2.857 (2) and 2.833 (2) Å, the latter distance being the shortest Pt–Pt distance characterized in a 1-D salt. (4) The Pt coordinates are (0, 0, 0), ±(−0.0053, 0.0021, 0.2516), and (0, 0, ½). (5) The oxalate ligands are bidentate and are staggered (~45°) with respect to the ligands directly above and below it in the chain. However, all Pt(2) oxalate ligands are eclipsed (~5°), while Pt(1) and Pt(3) oxalate ligands are staggered (~90°), giving a staircase effect to the ligands (see Figure 2). This staggering of oxalate ligands allows a nominal amount of $p\pi$ overlap between orbitals of the same symmetry and may account for the stabilization of the higher oxidation state and the decreased Pt–Pt separation. (6) Except for a single K^+ ion, all other K^+ ions and water molecules are positionally disordered. There are five K^+ ion sites and five H_2O sites in the asymmetric unit. (7) As is shown in Figure 3, the K^+ ion and water molecule interactions cause the exterior oxygens of the oxalate ligands to be bent from planarity. (8) An oxidation state of 2.4 for Pt is indicated by the crystallographic stoichiometry and is in good agreement with that found by chemical analysis.[11]

The true superlattice reflections persist to very high 2θ angles (160°, CuKα), giving evidence of their origin in scattering from Pt atoms. The supercell becomes commensurate with the intermediate cell at 116.19 Å, which delineates a 41 Pt atom repeat. It seems probable that errors in stacking of the bisoxalatoplatinum groups are responsible for the extended repeat. Since the two independent Pt–Pt distances are substantially unequal, stacking errors occurring at regular intervals will produce a modulated pattern of longitudinal Pt displacements. The modulated cell would become commensurate with the normal cell in a relation determined by the stacking defect frequency. An alternative view is that the two unequal Pt–Pt separations are but an artifact due to lack of inclusion of the superlattice intensities in the analysis. This view is difficult to reconcile with the persistence of superlattice intensity to large scattering angle. Clearly a complete structure analysis utilizing the superlattice intensities is required to establish a detailed model.

Acknowledgment. The authors wish to thank Professor Melvyn R. Churchill and Dr. Barry DeBoer for the use of their Picker diffractometer and assistance in the small cell data collection. We would also like to thank Mr. Don Washecheck[12] for doing the density measurement.

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(12) Participant in the Undergraduate Research Participation Program sponsored by the Argonne Center for Educational Affairs.

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Energy Upconversion and the Minimum Quantum Requirement in Photosynthesis[1]

Sir:

It was proposed in 1974 that the primary light reaction in photosynthesis is activated by a singlet–triplet annihilation mechanism whereby the initial photoexcitation in the far-red

wavelength region (680–700 and 870 nm in plant and bacterial photosynthesis, respectively) is upconverted to a two-photon equivalent.[2] Singlet–triplet annihilation interactions have long been recognized as an important photophysical process in the chlorophyll.[3] A recent study based on triplet absorption measurements[4] concluded that singlet–triplet annihilation is a dominant quenching mechanism for the lowest triplet T_1.[5] In this communication we examine the validity of energy upconversion postulate in terms of the latest experimental observations on the energy requirement for the primary light reaction, and reexamine the fundamental question of the quantum requirement in photosynthesis.

According to the energy upconversion theory[2] of photosynthesis, the primary processes leading up to the light reaction can be restated in terms of the most probable fate of the singlet S_1 excitation:

light harvest

$$2S_0 + 2h\nu \rightarrow 2S_1 \quad (1)$$

energy transfer and intersystem crossing of the first S_1 excitation to the lowest triplet T_1

$$S_1 \rightarrow T_1 \quad (2)$$

upconversion to a charge transfer (CT) state

$$S_1 + T_1 \rightarrow S_0 + CT \quad (3)$$

The photooxidation of the reaction center aggregate {Chl a}[6-10] by the primary electron acceptor A presumably follows the upconversion reaction 3. The reaction center radical cation {Chl a}$^+$ can be reduced by the primary donor either in the S_1 or the S_0, making available a choice of two photon "pumps":

$$\text{one-photon pump} \quad CT \rightarrow S_1 + \text{red chemistry} \quad (4)$$

$$\text{two-photon pump} \quad CT \rightarrow S_0 + \text{blue chemistry} \quad (5)$$

The conversion in eq 5 amounts to the transformation of two red photons into their additive free energy equivalent. The quantum requirement in this case is therefore two quanta per primary event. The regeneration of {Chl a} in S_1 in eq 4 leads to the conversion of one red photon into its free energy equivalent. The quantum requirement of this process is expected to be one quantum per primary event under steady-state operation because the S_1–T_1 upconversion rate should be much greater than the decay rate of the T_1 in {Chl a}. In effect the first trapped excitation will not be allowed to return to the ground state, and is recycled between the T_1 and CT manifolds.[2] The last condition would be ensured by the presence of a large number of antenna Chl a and accessory pigment molecules.

The existence of two separate photosystems (PS) in plant photosynthesis has been elucidated from several points of view. In particular the physical separation of two photosystems from in vivo organisms[11] and the spectroscopic identification of the P700 (PSI)[12] and P680 (PSII)[13] photoactive centers give rather convincing support for the two-photosystem proposal made by Hill and Bendall[14] based on biochemical evidence. The overall photosynthesis reaction amounts to the transfer of four hydrogen atoms from H_2O to CO_2 in order to reduce the latter to the emf level of carbohydrate:

$$CO_2 + 2H_2O \rightarrow (CH_4O_2) \equiv [(CH_2O) + H_2O)] + O_2 \quad (6)$$

The operation of two photosystems in series, assuming the widely accepted 1 quantum/electron requirement amounts to the requirement of 2 quanta/H atom transfer, or 8 quanta/O_2 liberated in eq 6.[15]

In the simpler picture of bacterial photosynthesis, there is only one photosystem characterized by the P870 reaction center.[15] It is generally believed, as in the case of photosynthesis in higher plants, that the quantum requirement for the primary reaction is 1 quantum/electron.[15] However, surprisingly, the measured quantum requirement for the overall process is 8 quanta/CO_2 reduced.[16] This quantum requirement implies that 2 quanta are needed for the transfer of one hydrogen atom. The accepted position in effect allows only one out of every two primary photoacts to be engaged in the transfer of one hydrogen atom while the other is wholly consumed in energizing cyclic photophosphorylation.[17] However, it is difficult to conceptualize the specificity of the two secondary pathways without invoking a two-photosystem model.

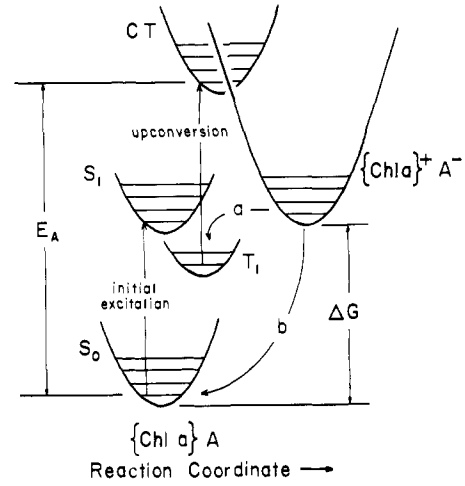

Figure 1. Free energy diagram illustrating the Franck–Condon principle in photosynthesis and the two possible cyclic pumps in the light reaction. ΔG is the free energy change of the primary event. For the back reaction {Chl a}$^+$ A^- → {Chl a} A, the a and b arrows represent the recycling pathways of the one-photon and two-photon pumps, respectively. In PSI, the reaction coordinate of {Chl a}$^+A^-$ is given by the photoenolization pathway of (Chl a·H_2O)$_2$ as described in ref 2, pp 257–260. This coordinate intersects the nuclear coordinate of Ct in the keto configuration of (Chl a·H_2O)$_2$ (see ref 7d). E_A is the maximum available free energy equivalent in the activation process.

Recently, Dutton et al. reported that the minimum energy required for the picosecond event of charge separation in $P870^+$ A^- is at least 1 eV.[18] Since the average energy of the incident light is about 1.4 eV (at 870 nm), it is clear that the average excitation energy after the usual 70% thermodynamic correction[19-21] has barely sufficient free energy (about 0.98 eV) to get the primary reaction started even if one assumes zero intersystem crossing to T_1. In addition, of course, the maximum available energy from the initial excitation must be further downgraded in view of the considerable Stokes shift. The fluorescence of P870 has a maximum at 910 nm.[22] If the minimum free energy requirement of 1 eV for the primary event is correct, therefore, it would appear obligatory to conclude that the upconversion mechanism is responsible for bacterial photosynthesis. In this case, we can readily account for the 8 quanta/CO_2 reduced requirement within the accepted one-photosystem model for bacterial photosynthesis by invoking the blue photon pump mechanism given in reaction 5, leading to the 2 quanta/electron requirement.

The preceding discussion has been based on a thermodynamic argument for the free energy equivalent of the excitation photon. The energy upconversion requirement in photosynthesis can be further explained in terms of the Franck-Condon principle in the photoactivation of the primary light reaction. Electronic transitions occur vertically along the vibrational coordinate because electronic motions are much faster than nuclear motions. Each electronic state can be described by a potential energy curve along some nuclear normal mode coordinate of the molecular complex. The coordinate we are interested in is the reaction coordinate along which the P870, for example, passes on an electron to its acceptor (see Figure

1). The potential surface of each state can thus be represented as a simple harmonic curve. The physical states of P870 can be represented by a set of more or less similar harmonic potentials whose minima are only slightly displaced with respect to each other because different electronic states of the neutral complex should not have much influence in changing the environment. The potential curve for $P870^+ A^-$, however, is strongly displaced from those of the neutral P870 curves because the charge separation in $P870^+ A^-$ is expected to cause a large reorganization in the surrounding membrane in which the $P870^+ A^-$ complex is presumably embedded. It thus becomes clear that if the thermodynamic (equilibrium) energy separation of P870 A and $P870^+ A^-$ is more than 1 eV, the initial excitation of the $P870^+ A^-$ state must be considerably greater.

The picture that emerges here can be described as follows. The $P870^+ A^-$–protein complex is created in an excited vibrational state. If the membrane were like an ordinary lattice one would expect this excess vibrational energy to become thermalized as the $P870^+ A^-$ complex settles down about its equilibrium position ($\gtrsim$1 eV above the ground state). The measurement on the *Rps. sphaeroides* reaction center by Dutton et al.[18] indicates that this vibrational decay occurs within 10^{-11} s. During this time span it is conceivable that the photoenergized membrane may become coupled in some specific pathway to some secondary mechanism for phosphorylation. In this way the upconversion mechanism in the primary light reaction is envisaged to generate not only the $P870^+ A^-$ complex but also provide a primary mechanism for energizing photosynthetic membranes.

It is generally accepted that the photosystem I in plant photosynthesis is closely analogous to the bacterial photosystem. If we apply comparative biology in the present context, we are tempted to conclude from the above discussion of bacterial photosynthesis that each of the two photosystems in higher plants may also observe the 2 quanta/electron requirement. This conclusion amounts to a theoretical 16 quanta/O_2 limit in the overall quantum requirements. In view of the frequently observed 10–12 quanta/O_2 requirement,[23] however, we cannot rule out the possibility that photosynthesis is powered by two photosystems, one operating as a blue photon pump (2 quanta/electron) and the other a red pump (1 quantum/electron). Given the balance of the available evidence either of these two alternatives would seem to be more likely than the existing two-photosystem model requiring the traditional 8 quanta for the evolution of one O_2 molecule.[24]

There is no evidence to support the widely accepted 1 quantum/electron requirement in the in vivo light reaction. The most recent measurements for the O_2 evolution quantum requirement in plant photosynthesis lies on the high side of the 10–12 range.[25] Reports of the observation[26] that chloroplast reactions sensitized exclusively by "purified" PSI proceed more efficiently in far-red light than in red light are difficult to rationalize in view of the well-established "red drop" in the quantum yield of O_2 evolution in plant photosynthesis. Likewise the observation[27] of 1 quantum/electron transfer requirement for cytochrome *c* and bacterial reaction center is in apparent conflict with the observed in vivo 2 quanta/H atom transfer requirement. Aside from the experimental difficulties,[28] the relevance of measurements on chemically modified reaction centers must be considered critically. Clearly the choice of the one- or two-photon pump cycle in eq 4 or 5 must depend on the electron donor.

For decades the determination of the minimum quantum requirement in photosynthesis from a purely empirical point of view has been a source of continuous (and at times bitter) debate.[23] The early controversy over the 4 quanta/O_2 requirement raged[23] prior to the establishment of the two-photosystem model in photosynthesis. The current paradigm of the 8 quanta/O_2 requirement (in spite of the repeatedly observed[23,25] values in the 10–12 range and the accepted[16,17] 8 quanta/CO_2 requirement in bacterial photosynthesis) has been developed before the incorporation of the well-established Chl a singlet–triplet annihilation interactions[3,5] into a molecular model for the primary light reaction.[2] It appears reasonable to assume that a proper description of photobiological processes need not invoke totally new physicochemical phenomena.[29] In this sense we believe that the present analysis provides a logical framework within which the interpretation of existing and future experimental observations should be based.[30,31]

Note Added in Proof: We note that the interpretive difficulties described by Warden (*Proc. Natl. Acad. Sci. U.S.A.*, **73,** 2773 (1976)) may be readily resolved by invoking the blue photon pump mechanism in reaction 5.

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(28) Serious errors in quantum yield determinations based on absorption and fluorescence spectra arise from numerous origins. Important sources include the lack of knowledge of the absolute extinction coefficients and, indeed, the absorbing species itself. Another reason for the large uncertainty in the determination of "absolute" quantum requirement is the need to extrapolate the observed data to the zero-intensity limit in order to avoid saturation effects.
(29) The acceptance of the 1 quantum/electron requirement leading to the conclusion of near 100% conversion efficiency for the Chl a S_1 excitation (see, for example, Chapter 3, ref 15) is tantamount to the assumption of zero quenching of S_1 by T_1. Where resonance conditions for S_1–T_1 annihilation prevail as in the case of Chl a,[3-5] such an assumption would be somewhat analogous to the treatment of condensed water in terms of the ideal gas behavior.

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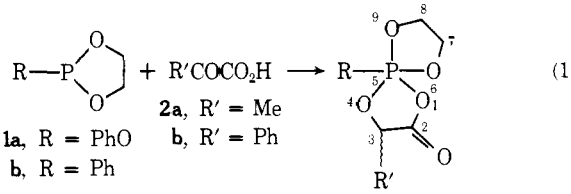
A New Route to Pentacovalent Cyclic Acyloxyphosphoranes

Sir:

The chemistry of pentacovalent oxyphosphoranes is currently one of the most active research fields.[1] These phosphorus compounds are closely related to reactions of the biologically important phosphate esters. For example, a pentacovalent cyclic acyloxyphosphorane has been implicated as an intermediate in the hydrolysis of phosphoenolpyruvate.[2] It becomes important, therefore, to prepare well-defined species of cyclic acyloxyphosphoranes and to examine their chemical reactivities. The present paper discloses a new synthetic method and the isolation of pentacovalent cyclic acyloxyphosphoranes, **3a–3d,** which are pentaoxy- and tetraoxyphosphorane derivatives. The reaction (eq 1) involves a hydrogen-transfer process of α-keto acids (**2**).



(1)

3a, R = PhO; R′ = Me
b, R = PhO; R′ = Ph
c, R = Ph; R′ = Me
d, R = Ph; R′ = Ph

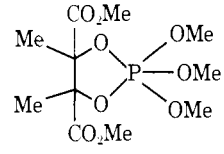
Into 20 ml of diethyl ether containing 3 mmol of 2-phenoxy-1,3,2-dioxaphospholane (**1a**) was added 3 mmol of pyruvic acid (**2a**) at 0 °C under nitrogen, and then the mixture was allowed to react at room temperature for 15 h. The mixture was further kept at −20 °C for 2 weeks in order to crystallize the product. The crystalline material was separated after washing with a small amount of diethyl ether and dried in vacuo to give 0.25 g (31% yield) of the product: mp 87 °C (from diethyl ether, hygroscopic); ir (KBr) 1745 (ν(C=O)), 1220 (ν(P—O—Ph)), 1035 (ν (P—O—CH_2)) cm^{-1} and no band at 1300–1250 cm^{-1} due to ν(P=O); ^1H NMR ($CDCl_3$, Me_4Si) δ1.57 and 1.62 (two d, 3H, CH_3, J_{HCCH} = 7 Hz),[3] 3.5–4.5 (m, 4 H, OCH_2CH_2O), 4.5–4.8 (m, 1 H, OCOCHO), 6.7–7.5 (m, 5 H, C_6H_5O). Anal. Calcd for $C_{11}H_{13}O_6P$: P, 11.38. Found: P, 10.91. All the above data support the structure of 2-oxo-3-methyl-5-phenoxy-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (**3a**).

The ^{31}P NMR gave additional support for the structure of **3a:** ^{31}P NMR (DMF, H_3PO_4 external) +39.7 and 36.5 ppm (relative intensity, 2.3:1.0).[3] The chemical shift of ^{31}P NMR is quite reasonable for the pentaoxyphosphorane structure having spiro ring system **3a.**[1a,4]

Similarly, the reaction of **1a** with phenylglyoxylic acid **2b** in a diethyl ether–hexane (5:3) mixture gave hygroscopic, white crystals of **3b** in an isolated yield of 25%: mp 60–62 °C (hygroscopic); ir 1750 (ν(C=O)), 1210 (ν(C—O—Ph)), 1027 (ν(P—O—CH_2)) cm^{-1}; ^1H NMR (CD_3CN) δ 3.62–4.62 (m, 4 H), 5.78–5.84 (two d, 1 H, J_{POCH} = 12 Hz and 16 Hz),[3] 6.66–7.82 (m, 10 H); ^{31}P NMR (CH_3CN) a broad signal at +39.1 ppm.[1a] Anal. Calcd for $C_{16}H_{15}O_6P$: P, 9.27. Found: P, 8.84.

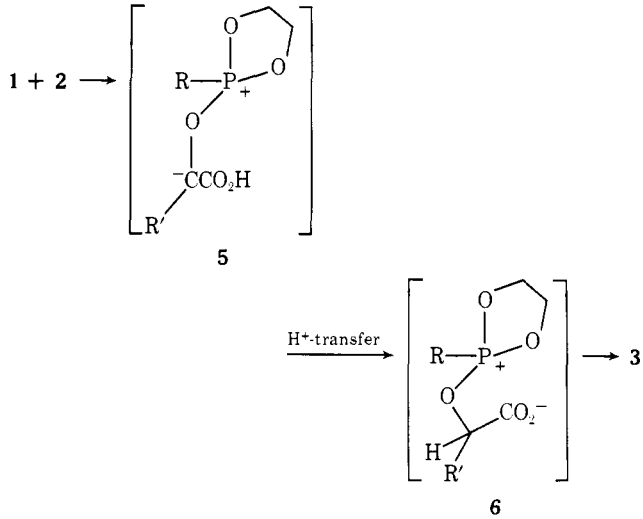
Reactions of 2-phenyl-1,3,2-dioxaphospholane (**1b**) with **2a** and **2b** also took place to produce **3c** and **3d,** respectively, in high isolated yields. The reaction of **1b** with **2a** (3 mmol each) in 15 ml of diethyl ether at room temperature yielded white crystalline product of **3c** (85% after 3 days): mp 56–58 °C (hygroscopic); ir (KBr) 1735 (ν(C=O)), 1035 (ν(P—O—CH_2)) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 and 1.62 (two d, 3 H, J_{HCCH} = 7 Hz),[3] 3.50–4.60 (m, 4 H), 4.72 (m, 1 H), 7.28–8.18 (m, 5 H); ^{31}P NMR (CH_3CN) +22.2 ppm.[1a] Anal. Calcd for $C_{11}H_{13}O_5P$: C, 51.57; H, 5.11; P, 12.09. Found: C, 51.78; H, 5.30; P, 11.31. The reaction of **1b** with **2b** occurred readily to give white crystals of **3d** (isolated in a 92% yield after 3 h at room temperature): mp 103–105 °C (ir (KBr) 1750 (ν(C=O)), 1040 (ν(P—O—CH_2)) cm^{-1}; ^1H NMR (CD_3CN) δ 3.53–4.60 (m, 4 H), 5.60 and 5.75 (two d, 1 H, J_{POCH} = 15 and 9 Hz),[3] 6.71–8.10 (m, 10 H); ^{31}P NMR (DMF) a broad signal at +22.0 ppm. Anal. Calcd for $C_{16}H_{15}O_5P$: C, 60.38; H, 4.75; P, 9.73. Found: C, 60.63; H, 4.92; P, 9.54.

Thus, the pentaoxy cyclic acyloxyphosphoranes, **3a** and **3b,** have been isolated for the first time as crystalline species. The isolated yields were higher with tetraoxyacyloxyphosphoranes, **3c** and **3d,** than with pentaoxy derivatives, **3a** and **3b.**[5] The present reaction (eq 1) involves the oxidation of **1** from trivalent to pentavalent and the reduction of **2** to an α-oxy acid derivative accompanying a hydrogen-transfer step. As to the reaction of eq 1, the following reaction should be cited. Trimethyl phosphate and 2 mol of methyl pyruvate (not pyruvic acid) reacted to give pentaoxyphosphorane **4,**[6] which is not a cyclic acyloxyphosphorane.



4

The formation of **3** from **1** and **2** probably involves an intermediate phosphonium carbanion **5,** which undergoes a hydrogen-transfer intra- and/or intermolecularly to yield a zwitterion **6.** Then, the cyclization of **6** leads to the product **3.**



5

6

The presence of the dioxaphosphorane ring in **1** markedly facilitates the ring closure of **6** to give a spiro compound **3.** The reaction of an acyclic phosphite **7** with **2a** however, gave **8** (22% yield), **9**[7] (64% yield), and presumably polymer **10.** No spirooxyphosphorane corresponding to **3** was obtained.