Table I. Dependence of Observed Pseudo-First-Order Rate Constants on Method of Stirring[a]

method of stirring[b]	swollen particle size, μm	10^5k_{obsd}, s^{-1} [e]
mechanical, 600 rpm	150-300	15
	100-200	21
vibromixer, upward[c]	150-300	15
vibromixer, downward[c]	150-300	14
	100-200	19
ultrasonic wave[d]	150-300	11

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst cross-linked by 2% divinylbenzene; 90 °C. [b] Photographs of the agitated reaction mixtures show that mechanical stirring breaks the organic phase into drops 0.5-3 mm in diameter dispersed in the aqueous phase, vibromixing produces much smaller but still visible organic droplets, and ultrasound produces an emulsion. [c] Two kinds of vibromixing were used. The disk with holes tapering upward forces the mixture to flow rapidly upward around the stirrer shaft. The disk with holes tapering downward forces the mixture to flow rapidly downward from the bottom of the disk. The vibrational amplitude was adjusted to prevent the catalyst from splashing out of the reaction mixture. [d] A 21-kHz probe was placed directly in the reaction mixture. Many of the catalyst particles formed large clusters. We suspect reduced activity of the clusters is responsible for the slower rate. [e] Rate constants are reproducible to ±5% with mechanical stirring and ±10% with vibromixing and ultrasonic mixing.

Table II. Dependence of Observed Pseudo-First-Order Rate Constants on Particle Size of Catalyst[a]

swollen particle size, μm	10^5k_{obsd}, s^{-1}
150-300	15
100-200	21
50-90	31
20-50	38
5-35	40

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst cross-linked by 2% divinylbenzene; 90 °C; 600-640 rpm mechanical stirring.

that the rate of ion exchange does not limit the kinetics. Rates were linearly dependent on the amount of catalyst from 0 to 4 mol %. With no catalyst, no reaction was observed in 24 h. Rate constants were reproducible to ± 5%.

Plots of pseudo-first-order rate constant vs. stirring speed are shown in Figure 1. The rate constants attained with 600 rpm mechanical stirring were as high or higher than those attained by turbulent mixing with a vibromixer or with an ultrasonic probe (Table I). Dependence of reaction rate on speed of stirring and method of mixing indicates that mass transfer contributes to rate limitation in the mechanically stirred mixtures at <600 rpm. Similar dependence of rate on magnetic stirring speed was reported for reactions of 1-bromooctane with iodide ion[4] and 1-decyl methanesulfonate with chloride ion.[5]

Particle size of a heterogeneous catalyst may strongly affect its activity.[7] Table II shows increasing rates with decreasing particle sizes of otherwise identical 2% cross-linked phosphonium salt catalysts. All of these catalysts are spherical particles obtained by suspension polymerization, not ground powders.[8] Their sizes were measured during microscopic examination of catalysts recovered from the reaction mixtures. If mass transfer limits reaction rates, smaller particles will be more active catalysts because of their greater surface area per catalytic site. If diffusion through the polymer matrix limits the rates, smaller particles will be more active because they offer shorter diffusion paths to the active sites. The particle size effect with mechanical stirring at 600 rpm, where mass transfer no longer limits the reaction rate, indicates that intraparticle diffusion contributes to rate limitation.

Table III. Effect of Structure and Content of the Cross-Linker on Observed Pseudo-First-Order Rate Constants[a]

cross-linker	wt % (mol %)	10^5k_{obsd}, s^{-1}
divinylbenzene	2	21
divinylbenzene	4	17
divinylbenzene	6 (5.3)	16
divinylbenzene	10	9.1
1,6-hexanediol dimethacrylate	(5.3)	18
1,10-decanediol dimethacrylate	(5.3)	18

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the catalyst; 90 °C; 600-650 rpm mechanical stirring. The catalysts were prepared from copolymers of particle size 75-150 μm.

With benzyltri-*n*-butylphosphonium chloride catalysts prepared from copolymers containing 2-10% divinylbenzene, the observed rate decreases as the degree of cross-linking increases (Table III). When aliphatic bis(methacrylates) instead of divinylbenzene are used in the copolymers, reaction rates increase slightly. These results also indicate that diffusion of reactant through the polymer matrix limits the reaction rates.

The structure of the active catalytic site also affects rates in our experiments, as it has in many previous studies.[1-5,9] Use of a 150-300-μm 2% divinylbenzene-cross-linked benzyltrimethylammonium chloride catalyst gave $k_{obsd} = 1.26 \times 10^{-5}\ s^{-1}$ with 600 rpm mechanical stirring compared with $k_{obsd} = 15 \times 10^{-5}\ s^{-1}$ for the benzyltri-*n*-butylphosphonium chloride catalyst made from the same copolymer.

In summary, mass transfer and intraparticle diffusion as well as the catalyst structure influence the rate of phase-transfer reaction of cyanide ion with 1-bromooctane when benzyltri-*n*-butylphosphonium salt catalysts bound to 2-10% cross-linked polystyrene are employed. Studies of the key experimental parameters affecting rates of other phase-transfer reactions and use of other polymer-supported catalysts are in progress.

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(7) Satterfield, C. N. "Mass Transfer in Heterogeneous Catalysis"; M.I.T. Press: Cambridge, MA, 1970; Thomas, J. M.; Thomas, W. J. "Introduction to the Principles of Heterogeneous Catalysis"; Academic Press: New York, 1967; Chapter 4; Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; Chapter 11.

(8) A fine powder (<45 μm) produced by *grinding* showed very low activity ($k_{obsd} = 2.4 \times 10^{-5}\ s^{-1}$). Similar decreases in rate with ground powders have been observed by Regen.[3] Spherical catalyst particles settle quickly to the phase interface when mixing stops, but irregular particles obtained by grinding remain suspended in the organic phase much longer. We attribute the slower rate with ground powder to insufficient contact between the catalyst and the aqueous phase.

(9) (a) Chiles, M. S.; Reeves, P. C. *Tetrahedron Lett.* **1979**, 3367. (b) Tundo, P.; Venturello, P. *J. Am. Chem. Soc.* **1979**, *101*, 6606. (c) Regen, S. L.; Nigam, A. *Ibid.* **1978**, *100*, 7773. (d) Tundo, P. *Synthesis* **1978**, 315.

(10) On leave 1979-1980 from Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama 240, Japan.

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Structure and Stereochemistry of Novel Endoperoxides Isolated from the Sensitized Photooxidation of Methyl Linoleate. Implications for Prostaglandin Biosynthesis

Sir:

Evidence continues to accumulate supporting the involvement of singlet molecular oxygen ($^1O_2$) during lipid oxidation in vegetable oils[1,2] and complex biological systems.[3] Although the reaction of $^1O_2$ with polyunsaturated fatty acids to yield allylic hydroperoxides[4] is well documented, we are unaware of any study

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(1) Frankel, E. N.; Neff, W. E.; Bessler, T. R. *Lipids* **1979**, *14*, 961-967 and references cited.

(2) Yamauchi, R.; Matsushita, S. *Agric. Biol. Chem.* **1979**, *43*, 2157-2161.

(3) See: Krinsky, N. I. In "Singlet Oxygen"; Wasserman, H. H., Murray R. W., Eds.; Academic Press: New York, 1979; Chapter 12.

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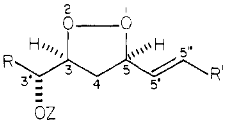
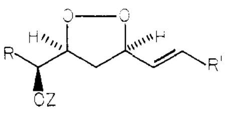
which has attempted to fully characterize the more polar secondary oxidation products common to these reactions. We now report the formation of 1,2-dioxolanes during the dye-sensitized photooxidation of methyl linoleate [(*Z*,*Z*)-9,12-octadecadienoic acid methyl ester] which arise from an alkenylperoxy radical cyclization that is stereochemically analogous to that thought to occur during prostaglandin biosynthesis.[5]

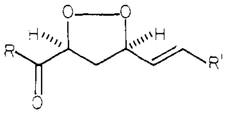
Sensitized photooxidation of neat methyl linoleate (Rose Bengal, O_2, tungsten light)[6] afforded the known monohydroperoxides[4] (R_f 0.33, 70%) and two more polar products, **1** (R_f 0.20, 7%) and **2** (R_f 0.16, 5%), which were isolated by medium-pressure liquid chromatography.[7,8] Extensive spectral characterization of these materials[9,10] supported assignment of the α-hydroperoxy-3,5-disubstituted-1,2-dioxolane structures; however, the relative configurations of the three chiral centers could not be deduced with certainty. Each diastereomer was individually reduced with trimethyl phosphite (1 equiv) to give alcohols **3** and **4** (70% yield after chromatography).[9,11] Oxidation of each of these with pyridinium chlorochromate produced the same ketone **5**,[9,11] indicating the two series of compounds were epimeric at C-3′. The facile separation of the positional isomers of **4** by medium-pressure LC allowed determination of complete relative stereochemistry. Hydrogenation (PtO_2/CH_3OH) of the more polar isomer, **4a**, produced trihydroxy methyl stearate **6a** which was identical[12] with an authentic sample of (9*R*,10*R*,12*R*)-methyl 9,10,12-trihydroxyoctadecanoate prepared from ricinoleic acid.[13,14] These data firmly establish the stereochemical features of **1** and **2** as shown.



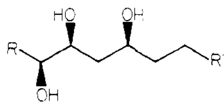
1, Z = OH
3, Z = H



2, Z = OH
4, Z = H



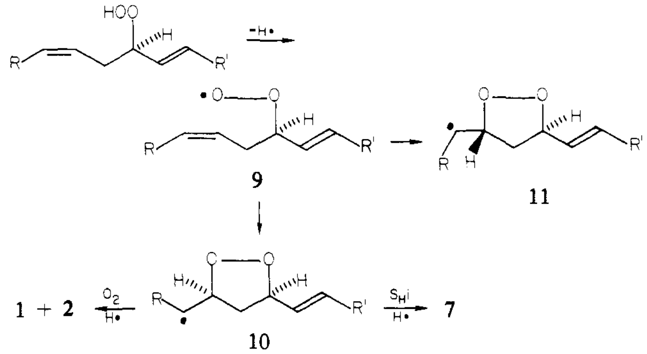
5



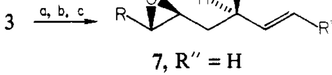
6

a, R = $(CH_2)_7CO_2CH_3$, R′ = $(CH_2)_3CH_3$
b, R = $(CH_2)_4CH_3$, R′ = $(CH_2)_6CO_2CH_3$

Scheme I



Autoxidation (O_2, EtOAc, room temperature, 2 h) of the monohydroperoxide fraction recovered from the $^1O_2$ reaction also produced considerable amounts of diperoxides **1** and **2**. In addition, a new, more polar product was formed in approximately equal quantity. Spectral data[9,11] suggested it was an unsaturated epoxy alcohol which was predominantly a *single diastereomer*. Assignment of the complete structure as **7** was achieved by synthesizing authentic material from **3** as shown in the equation. The two samples so obtained were indistinguishable as both the free alcohol **7** and acetate derivative **8**.[12]



7, R″ = H
8, R″ = $COCH_3$

(a) MesCl, Et_3N, CH_2Cl_2; (b) $SnCl_2$, CH_3OH; (c) *t*-BuOK, Et_2O

The oxidation products that we have isolated can be derived from the initially formed nonconjugated diene hydroperoxides by the autoxidation pathways summarized in Scheme I. Formation and ring closure of β,γ-unsaturated peroxy radicals is a well-known event.[15] Our data indicate that in unsaturated fatty acid systems a highly selective ring closure occurs, affording radical **10** possessing the *cis*-1,2-dioxolane ring. Reaction of **10** with molecular oxygen leads to **1** and **2** whereas backside attack of the radical on the peroxide bond yields **7**.[16] It is clear from our stereochemical findings that **1**, **2**, and **7** must all originate from the common intermediate **10**.

trans-Dioxolanes, which would result from intermediate **11**, were not found in other chromatographic fractions. However,

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(4) For example, photosensitized oxidation of methyl linoleate yields four isomeric monohydroperoxides (9-$\Delta^{10,12}$; 10-$\Delta^{8,12}$; 12-$\Delta^{9,13}$; 13-$\Delta^{9,11}$). See: Gollnick, K.; Kuhn, H. J. in ref 3, Chapter 8, p 350.

(5) (a) Samuelsson, B. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* **1972**, *31*, 1442–1450. (b) Sih, C. J.; Takeguchi, C. A. In "The Prostaglandins"; Ramwell, P. W., Ed.; Plenum Press: New York, 1973; Vol. 1, Chapter 3.

(6) Cobern, D.; Hobbs, J. S.; Lucas, R. A.; MacKenzie, D. J. *J. Chem. Soc. C* **1966**, 1897–1902.

(7) All compounds described in this study are racemic and consist of an equal mixture of positional isomers a and b except where noted otherwise.

(8) Thin-layer chromatography (TLC) was done on silica gel, eluting with 25% ether in pentane.

(9) All NMR spectra were taken in dilution solutions of deuteriochloroform and are referenced to tetramethylsilane internal standard. Proton assignments have been fully substantiated by homonuclear decoupling experiments; carbon assignments were confirmed by selective ^1H-decoupling techniques. These data are for mixtures of a and b isomers. **1**: IR (CCl_4) 3542 (w), 3400 (s), 1738, 968 cm^{-1}; ^1H NMR (100 MHz) δ 9.4 (br s, 1, OOH), 5.91 (dt, 1, *J* = 15, 6 Hz, H-5″), 5.66 (dd, 1, *J* = 15, 7.5 Hz, H-5′), 4.70 (q, 1, *J* = 7.5 Hz, H-5), 4.44 (ddd, 1, *J* = 8, 5.5, 4 Hz, H-3), 4.12 (m, 1, H-3′), 3.66 (s, 3, $-OCH_3$), 2.82 (ddd, 1, *J* = 12, 8, 7.5 Hz, H-$_4\beta$), 2.43 (ddd, 1, *J* = 12, 8, 5.5 Hz, H-4α); ^{13}C NMR (22.5 MHz) 174.3 (CO_2CH_3), 139.3, 139.0 (C-5′), 124.3, 124.1 (C-5″), 86.0 (C-3′), 83.6 (C-3), 83.1 (C-5), 51.42 (CO_2CH_3), 41.2 (C-4) ppm. **2**: IR (CCl_4) 3540 (w), 3420 (s), 1738, 968 cm^{-1}; ^1H NMR (300 MHz) δ 9.3 (br s, 1, OOH), 5.87 (dt, 1, *J* = 15.5, 6.5 Hz, H-5″), 5.40 (dd, 1, *J* = 15.5, 7.5 Hz, H-5′), 4.66 (q, 1, *J* = 7.5, H-5), 4.50 (ddd, 1, *J* = 7.5, 7.0, 6.0 Hz, H-3), 3.95 (m, 1, H-3′), 3.66 (s, 3, $-OCH_3$), 2.82 (ddd, 1, *J* = 12, 7.5, 7 Hz, H-4β), 2.16 (ddd, 1, *J* = 12, 7.5, 6.0 Hz, H-4α); ^{13}C NMR (20 MHz) 174.3 (CO_2CH_3), 139.0, 138.7 (C-5′), 124.45, 124.2 (C-5″), 85.75 (C-3′), 83.5 (C-3), 82.75 (C-5), 51.46 (CO_2CH_3), 43.25 (C-4) ppm. **3**: IR (CCl_4) 3570, 1738, 968 cm^{-1}; ^1H NMR (100 MHz) δ 5.84 (dt, 1, *J* = 15.5, 6.5 Hz, H-5″), 5.42 (dd, 1, *J* = 15.5, 7.75 Hz, H-5′), 4.66 (q, 1, *J* = 7.5 Hz, H-5), 4.26 (ddd, 1, *J* = 8, 6.25, 3.75 Hz, H-3), 3.86 (m, 1, H-3′), 2.69 (ddd, 1, *J* = 12, 8, 7.5 Hz, H-4β), 2.45 (ddd, 1, *J* = 12, 8, 6.25 Hz, H-4α); ^{13}C NMR (20 MHz) 174.3 (CO_2CH_3), 138.4, 138.1 (C-5′), 124.9, 124.6 (C-5″), 84.2 (C-3), 82.84 (C-5), 71.84 (C-3′), 51.42 (CO_2CH_3), 40.4 (C-4) ppm. **4**: IR (CCl_4) 3575, 1738, 968 cm^{-1}; ^1H NMR (300 MHz) δ 5.86 (dt, 1, *J* = 15.5, 6.5 Hz, H-5″), 5.38 (dd, 1, *J* = 15.5, 7.75 Hz, H-5′), 4.64 (q, 1, *J* = 7.5 Hz, H-5), 4.18 (ddd, 1, *J* = 7.75, 6.5, 5.25 Hz, H-3), 3.66 (s, 3, $-OCH_3$), 3.57 (m, 1, H-3′), 2.78 (dd, 1, *J* = 12, 7.75, 7.5 Hz, H-4β), 2.14 (ddd, 1, *J* = 12, 8.25, 5.25 Hz, H-4α); ^{13}C NMR (20 MHz) 174.1 (CO_2CH_3), 138.7, 138.4 (C-5′), 124.3, 124.0 (C-5″), 84.5 (C-3), 82.7 (C-5), 72.67 (C-3′), 51.25 (CO_2CH_3), 42.7 (C-4) ppm. **5**: IR (CCl_4) 1740, 1720, 962 cm^1; ^1H NMR (60 MHz) δ 5.84 (dt, 1, *J* = 15.5, 6 Hz, H-5″), 5.22 (dd, 1, *J* = 15.5, 7 Hz, H-5′), 4.58 (m, 2H, H-3 and H-5), 3.66 (s, 3, $-OCH_3$); ^{13}C NMR (20 MHz) 211.5 (C=O), 174.26 (CO_2CH_3), 139.7, 139.45 (C-5′), 123.8, 123.6 (C-5″), 84.95 (C-3), 82.34 (C-5), 51.4 (CO_2CH_3), 43.2 (C-4) ppm. **7**: IR (CCl_4) 3620, 3520, 1740, 970 cm^1; ^1H NMR (90 MHz) δ 5.6 (m, 2), 4.3 (m, 1), 3.66 (s, 3), 2.75 (m, 2); ^{13}C NMR (22.5 MHz) 174.25 (CO_2CH_3), 132.7, 132.5, 132.2, 132.1, 71.4 (C–OH), 58.6, 56.3, 51.4 (CO_2CH_3), 39.7 ppm.

(10) Chemical ionization mass spectrometry using ammonia as reagent gas (NH_3–CI) gave two intense peaks: *m*/*e* (rel. intensity) 376 [$(M + 18)^+$, 88.7], 358 [$(M + 18 - H_2O)^+$, base peak].

(11) NH_3–CI gave a base peak of $(M + 18)^+$ for this compound.

(12) IR, TLC, and ^1H and ^{13}C NMR comparisons were made.

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(14) EI GC/MS of the Me_3Si ethers of **6a** and **6b** derived from **4a** and **4b** confirmed that they were the 9, 10, 12 and 10, 12, 13 isomers, respectively.

(15) Porter, N. A.; Funk, M. O.; Gilmore, D. W.; Isaac, S. R.; Menzel, D. B.; Nixon, J. R.; Roycroft, J. H. In "Biochemical Aspects of Prostaglandins and Thromboxanes"; Kharasch, N., Fried, J., Eds.; Academic Press: New York, 1977, 39–53.

(16) (a) Porter, N. A.; Cudd, M. A.; Miller, R. W.; McPhail, A. T. *J. Am. Chem. Soc.* **1980**, *102*, 414–416. (b) Porter, N. A.; Nixon, J. R. *Ibid.* **1978**, *100*, 7116–7117.

faint absorptions at 136.6, 126.8, 85.1, 82.2, and 41.5 ppm in the ^{13}C NMR spectrum of **1** suggested the presence of a small amount of such an isomeric peroxide. Careful high-pressure LC (10% EtOAc/hexane, μ-Porasil) of this fraction resolved a minor, faster moving component from **1** whose spectral features were consistent with the missing *trans*-dioxolane fraction.[17] Quantitatively, it accounts for 5% of the total endoperoxide mixture (**1** + **2**), making the cis/trans selectively 19:1.

Although cis selectivity in alkenylperoxy radical cyclizations has just recently been reported,[18] the exceptional preference exhibited in the linoleate system and the similarity of these materials to the proposed intermediates in prostaglandin biosynthesis make our results especially noteworthy. We have also shown that hydroperoxides of the triunsaturated fatty ester, methyl linolenate, form *cis*-dioxolanes analogous to **1** and **2** with the same degree of selectivity.[19] We conclude that it is a general property of β,γ-unsaturated lipid hydroperoxides to cyclize stereoselectively to *cis*-1,2-dioxolanes and that this preference may be an implicit step in the enzymatic formation of prostaglandin endoperoxides.

Acknowledgment. I wish to thank Ms. Karen Daniels for technical assistance, Dr. J. P. Yesinowski and Mr. Doug Ingram for the 300-MHz ^{1}H NMR data, Dr. A. DeStefano and Dr. T. Keough for mass spectral analyses, and Dr. D. E. O'Connor for helpful discussions.

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(17) Only enough of this material could be collected for preliminary ^{1}H and ^{13}C FT-NMR evaluation. Comparison to model compounds proved helpful in this structure assignment and this work will be described in the full paper.

(18) Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099-7100.

(19) O'Connor, D. E.; Mihelich, E. D.; Coleman, M. C. unpublished results. Autoxidation and singlet oxygenation of methyl α-linolenate yielded two diastereomeric dioxolanes each of which consisted of 9,10,12 and 13,15,16 positional isomers.[20] Relative stereochemistry was strongly implicated by comparison of their NMR spectral features to those of **1** and **2** and proven by conversion to triols as described for the linoleate diperoxides. Autoxidation of 13-hydroxyperoxylinolenate (obtained from the action of soybean lipoxygenase on α-linolenic acid followed by diazomethane esterification) afforded two pure 16-hydroperoxy 13,15-endoperoxides. The major and less polar isomer has also been isolated by Chan[23] and can now be assigned the 13*S*,15*R*,16*S* configuration. The less abundant, more polar isomer has the 16*R* configuration.

(20) These compounds have TLC mobilities identical with those reported for cyclic peroxides isolated from both an enzymatic oxidation[21] and autoxidation[22] of methyl linolenate. Our results indicate that the claim of 1,2-dioxane formation in the latter case, which was based on some minor hydrogenation byproducts,[22] is in error. This is in agreement with the extensive model studies of Porter[15] where no trace of dioxane formation was observed even in "thermodynamically biased" cases.

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Primary Electron Acceptors in Plant Photosynthesis

Sir:

Recent spectroscopic evidence indicates that short-lived transients mediate the light-induced charge separation in photosystems (PS) I and II of plant photosynthesis.[1-8] These intermediates, labeled A_1 (first acceptor) in PS I and I (intermediary acceptor) in PS II, transfer an electron in a picosecond time domain from the chlorophyll phototraps to secondary acceptors, iron-sulfur proteins in PS I and plastoquinone (Q) in PS II. Chlorophyll *a* (Chl)[3-6,9-11] and pheophytin *a* (Pheo, a metal-free Chl)[6-8] have been proposed as A_1 and I, respectively. We present here electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) results which establish that in subchloroplast fragments enriched in PS II reaction centers, the trapped primary electron acceptor (I^-) exhibits magnetic characteristics (*g* value, ESR line width, saturation behavior, and ENDOR transitions) very similar to those of the monomeric anion radical of Pheo in vitro. In addition, the midpoint potential[12] and the optical changes[7,8,12] that accompany the reduction of I in vivo closely parallel those observed for monomeric Pheo in vitro.[6] We conclude that pheophytin *a* is the most likely candidate as the primary electron acceptor of the charge separation induced by light in PS II.

Parallel ESR and ENDOR results on subchloroplast fragments enriched in PS I, taken in conjunction with recent optical data obtained by picosecond[3-5] and other flash-kinetic[3,11] techniques, suggest that a monomeric chlorophyll[6] acts as the primary electron acceptor in PS I.

The intermediate I^- was trapped in subchloroplast fragments (TSF-IIa) highly enriched in PS II reaction centers[13] by a technique[8] which takes advantage of the fast reaction of endogenous donors (D) with P680$^+$, the phototrap of PS II. Under continuous illumination at 210 K and at redox potentials low enough to reduce the secondary acceptor Q (−0.45 V vs. NHE), the rapid, reversible photooxidation of P680

$$\text{D P680 I Q}^- \underset{2\text{–}4\ \text{ns}}{\overset{h\nu,\ S_2O_4^{2-}}{\rightleftarrows}} \text{D P680}^+\text{I}^-\text{Q}^-$$

is terminated by the eventual reduction of P680$^+$ by the donor D:

$$\text{D P680}^+\text{I}^-\text{Q}^- \xrightarrow[\leq 1\ \mu s]{} \text{D}^+\ \text{P680 I}^-\ \text{Q}^-$$

Under the strongly reducing conditions used, D$^+$ is reduced by the medium with the net photoreaction:

$$\text{D P680 I Q}^- \xrightarrow{h\nu} \text{D P680 I}^-\ \text{Q}^- + \text{oxidized medium (prepn A)}$$

If the photoillumination is carried out at 273 K, an additional product accumulates:

$$\text{D P680 I}^-\ \text{Q}^- \rightarrow \text{D P680 I Q}^{2-}$$

Repetition of the above reactions leads to a trapped I^-,Q^{2-} configuration:

$$\text{D P680 I Q}^{2-} \xrightarrow[273\ \text{K}]{h\nu} \text{D P680 I}^-\ \text{Q}^{2-}\ \text{(prepn B)}$$

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(13) The preparations, obtained by Triton treatment of spinach chloroplasts, contained ~1 PS II reaction center per 30-40 Chl molecules and were free of PS I reaction centers. The fragments were suspended in 0.1 M tricine-NaOH (pH 8) which contained 50% glycerol.[8]

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