Stereochemistry and Mechanism for the Palladium(II)-Catalyzed Oxidation of Ethene in Water (the Wacker Process)

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Abstract: Palladium(II)-catalyzed oxidation of specifically deuterated ethenes in water in the presence of cupric chloride and chloride ion has been studied. Stereospecific formation of *threo*-1,2-dideuterio-2-chloroethanol (*threo*-**3**) from (*E*)-1,2-dideuterioethene ((*E*)-**2**) indicates that the hydroxypalladation step in the Wacker oxidation is a trans process. Generation of an *erythro*-β-hydroxyethylpalladium complex (**6**) from *erythro*-β-hydroxyethylmercuric chloride (**5**) in the presence of $CuCl_2$–LiCl also results in the formation of *threo*-**3**. Analyses of the deuterated products were done by microwave spectroscopy. A new (modified) mechanism is proposed, which involves reversible formation of **11** by external attack of water on **8**, followed by a rate-determining dissociation of a chloride ligand from **11**.

Introduction

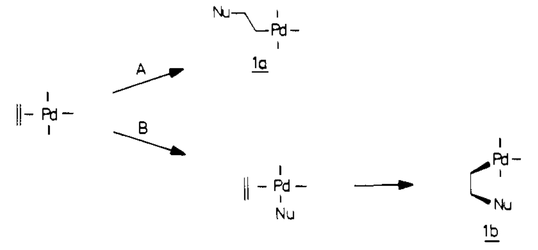
The success of the Wacker process[2] as an efficient industrial method for oxidation of ethene to acetaldehyde (eq 1) has initiated an intense study of palladium-catalyzed organic reactions.[3,4] Special interest has been devoted to reactions in which palladium(II) promotes nucleophilic addition to olefins and related unsaturated systems. This has led to the development of a number of palladium-promoted or -catalyzed reactions of olefins.[3-6] It is generally agreed that, in most reactions of this type, a σ complex **1**, usually unstable, is an intermediate.

$$CH_2=CH_2+\frac{1}{2}O_2\xrightarrow[CuCl_2]{PdCl_2}CH_3CHO \qquad \text{(eq 1)}$$

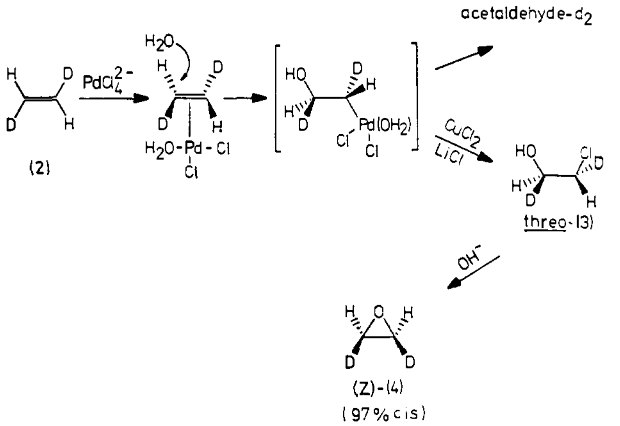
An important question concerning the mechanism of such reactions is the steric course of the addition of the metal and the nucleophile to the double bond (path A or B, Scheme I). Several studies have considered this question and, because different nucleophiles can add with different stereochemistry, there was originally some confusion and much speculation. More recently, however, the stereochemistry of such reactions has been studied directly. Thus palladium and nucleophiles like acetate,[7] methanol,[8,9] or amine[10] have been shown to add trans to olefins (path A), whereas palladium and nucleophiles such as aryl,[7b] alkyl,[7b] or methoxycarbonyl[8] have been shown to add cis (path B).

Although the mechanism of the Wacker oxidation of ethene to acetaldehyde has attracted considerable attention,[2,4,8-13] there is still disagreement about the steric course of the hydroxypalladation step (path A or path B, Scheme I). Kinetic studies suggest that a cis addition of Pd(II) and coordinated OH takes place,[4,7b,11-13] implying that the hydroxylation has a different steric course from the addition of other related nucleophiles. However, more recent studies by us[10] and others[8] suggest that also the Wacker hydroxylation might be a trans process. We therefore undertook a study on the mechanism of the Wacker hydroxylation with the aim to obtaining conclusive evidence for the steric course of the reaction. In a preliminary communication[14] we reported that trans-hydroxypalladation takes place, and on the basis of this finding we proposed a new mechanism. In the present paper we give a complete account of these results, discuss the new mechanism, and also present additional results which support the conclusions drawn in the earlier communication.

Scheme I



Scheme II



In the Wacker oxidation of ethene, the formation of chlorohydrin has been observed[2,15] which can be obtained as the main product by increasing the copper(II) and chloride ion concentrations.[15] It is reasonable to assume that the acetaldehyde and the 2-chloroethanol are formed from the same intermediate, a β-hydroxyethylpalladium complex (**1**, Nu = OH). β-Elimination gives the aldehyde and oxidative cleavage[16] the chlorohydrin (Scheme II). By determining the configuration of the chlorohydrin obtained from specifically deuterated ethene, we have thus been able to establish the steric course of the hydroxypalladation step.

Results and Discussion

The oxidation of (*Z*)- and (*E*)-ethene-d_2 was performed in aqueous solution of $PdCl_2$-$CuCl_2$-LiCl under pressure (≃3-5 kg/cm^2) (Scheme II). The LiCl concentration used was 3.3 M. The main products from these reactions were chloroethanol-d_2 (**3**) and acetaldehyde. The configuration of **3** was determined by microwave spectroscopy. The rotational transi-

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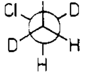
Table I. Rotational Transitions of **3**[a] Used for Analysis[b,c]

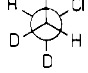
transition	*threo*-(A)-**3**[d]	*threo*-(B)-**3**	*erythro*-(A)-**3**	*erythro*-(B)-**3**
$7_{25} \leftarrow 7_{16}$	20607.02 (0.58)	20483.14	21106.39	19966.80
$8_{26} \leftarrow 8_{17}$	20354.11	20595.77 (1.19)	20940.21	19975.03
$14_{3,11} \leftarrow 14_{2,12}$	31617.31 (0.71)	31100.91	32155.69 ($\simeq$0.3)	30285.76
$15_{3,12} \leftarrow 15_{2,13}$	31053.84	31525.59 (1.02)	31822.50	30418.84 (0.63)
$18_{3,15} \leftarrow 18_{2,16}$	32166.13 (1.72)	37348.59 (3.16)	34249.85 (2.21)	34849.36 (2.78)

[a] Authentic samples were used for the recording of the spectra (see Experimental Section). [b] Frequencies of transitions are given in megahertz. [c] Only the gauche conformation of chloroethanol has been observed in the gas phase.[17] Owing to two energetically equivalent gauche confor-

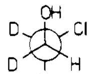
threo-(A)-3



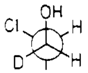
threo-(B)-3



erythro-(A)-3



erythro-(B)-3

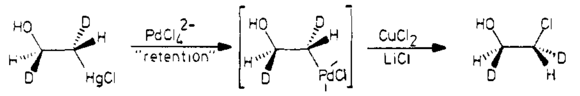


mations in each of *threo*-**3** and *erythro*-**3**, two different spectra were observed in each case. [d] The figures in parentheses indicate quadropole splitting. All of the lines chosen were either singlets or doublets. No figure means singlet.

tions used for this analysis are given in Table I. By treatment with hydroxide ion **3** was converted into the corresponding epoxide **4**, which was also analyzed by microwave spectroscopy. This conversion, which results in one inversion, was carried out in order to facilitate a more accurate quantitative analysis, the rotational transitions of **4** being much stronger than those of **3**. Transitions used for quantitative analysis of **4** are given in Table II. Microwave spectroscopy proved to be a convenient and powerful method for the analysis of **3** and **4**. The results from such an analysis are given in Table III. The chlorohydrin formed from (*E*)-**2** was found to be *threo*-**3** and the corresponding epoxide was (*Z*)-**4**. Similarly (*Z*)-**2** gave *erythro*-**3**. The extent of *Z*,*E* isomerization of ethene-d_2 was <1% during the reaction, as shown by conversion[19] of the recovered ethene into epoxide and subsequent microwave analysis.

The overall result is thus cis addition of hydroxyl and chloride. In a recent study it was shown by one of us[16] that the cleavage of a palladium-primary carbon bond by the $CuCl_2$–LiCl system results in inversion at carbon. Although this reaction was studied initially in acetic acid, the inversion mechanism resulting from S_N2 displacement by chloride ion should be even more pronounced in water. The results from such a cleavage in water (vide infra) confirm this conclusion. The conversion of (*E*)-**2** into *threo*-**3** and (*Z*)-**2** into *erythro*-**3** therefore shows that the hydroxypalladation step must be a trans process.

Here a control experiment is called for. It has recently been found[20] that intramolecular displacement of palladium by nitrogen takes place in aminopalladation adducts under oxidative conditions to give aziridines. An analogous reaction of the hydroxypalladation adduct, although very unlikely, via an epoxide must therefore be considered. If ethylene oxide were an intermediate, the present conclusion about the stereochemistry of the hydroxypalladation would be reversed. We therefore studied the reaction shown in eq 2. The mercury



(eq 2)

5 6 threo-3

40% (> 96% threo)

compound **5**, prepared from hydroxymercuration of (*E*)-**2**, was treated with the $PdCl_2$–$CuCl_2$–LiCl system used above for the oxidation of ethene. In this way **5** gave *threo*-**3** via the putative[21] intermediate **6**. Since (*E*)-ethene-d_2 ((*E*)-**2**) was the other main product, the chlorohydrin could in principle result from palladium catalyzed hydroxylation of (*E*)-**2**, the latter being formed from decomposition of **5**. However, we found, as also noted by others,[22] that this path would be too slow to account for the rapid formation of products. Thus only traces of chlorohydrin were formed in a control experiment when ethene was bubbled through a solution of the $PdCl_2$–$CuCl_2$–LiCl system for the same period of time as used for the conversion of **5** into *threo*-**3**. Further evidence for an intermediate **6** follows from the fact that **5** failed to give any chloroethanol in the absence of palladium, the $CuCl_2$ and LiCl concentrations being unchanged. Alkyl transfer from mercury to palladium is known[23] to take place with retention of configuration at carbon. Therefore the formation of *threo*-**3** from **5** excludes an epoxide intermediate, since the expected product from such an intermediate would have been *erythro*-**3**. The results also show that the cleavage of a primary palladium-carbon bond by $CuCl_2$–LiCl proceeds with inversion also in water solution.

Table II. Rotational Transitions of **4** Used for Analysis[a]

transition	(*Z*)-**4**, MHz	(*E*)-**4**, MHz
$3_{21} \leftarrow 3_{12}$	19252.85	19742.83
$4_{31} \leftarrow 4_{22}$	24407.89	25859.55
$6_{42} \leftarrow 6_{33}$	32116.10	34017.59
$7_{43} \leftarrow 7_{34}$	36874.02	37235.20

[a] The transitions measured by us are in perfect agreement with those reported.[18] The complete spectra of (*Z*)-**4** and (*E*)-**4** are given in ref 18.

The formation of (*E*)-**2** as a second major product may be of some relevance for the mechanism of the Wacker process. Although the ethene formed may have its origin in deoxymercuration of **5**,[24] it is tempting to speculate that formation of (*E*)-**2** occurs from the organopalladium intermediate **6**. The deoxypalladation of this intermediate would evidently proceed trans. This would be consistent with the suggestion that the hydroxypalladation is a reversible reaction.[14]

The kinetics of the Wacker process has been studied by several groups[2,4,11-13] and the rate expression, determined independently by these workers, is given in eq 3. The inverse

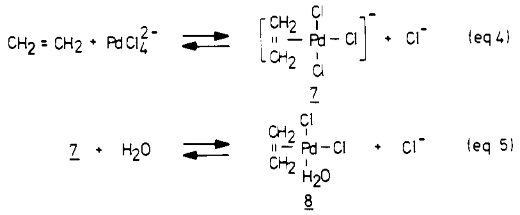
$$\frac{d[CH_3CHO]}{dt} = k\,\frac{[\text{ethene}]\,[PdCl_4^{2-}]}{[H^+]\,[Cl^-]^2} \qquad \text{(eq 3)}$$

square dependence on chloride and first-order dependence on ethene and $PdCl_4^{2-}$ are described by eq 4 and 5. There is general agreement about this interpretation of the dependence on the chloride, ethene, and palladium concentrations. However, the inverse dependence on acid can be explained in several ways. The interpretation commonly accepted[4,7b,11-13,25] leads to the mechanism shown in Scheme III. In this suggested[7b,11]

Table III. Hydroxychlorination of (*Z*)- and (*E*)-1,2-Dideuterioethene (**2**)[a]

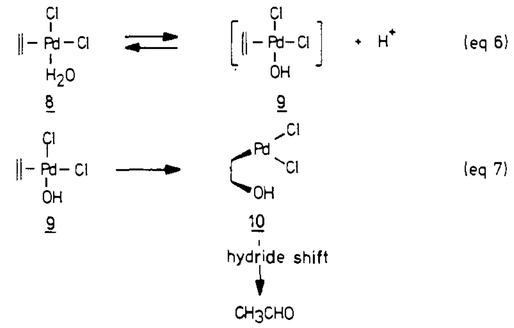
olefin	reaction time, h	initial gauche pressure of **2**, kg/cm^2	product **3**	conversion product	
				(*Z*)-**4**[b]	(*E*)-**4**[b]
(*E*)-**2**	32	5.0	threo[c]		
(*E*)-**2**	28	5.5		97	3
(*E*)-**2**	36	4.7		97.5	2.5
(*Z*)-**2**	30	4.9	erythro[d]		
(*Z*)-**2**	28	5.0		3	97

[a] Performed in water at 20 °C with the following concentrations: [$PdCl_2$] = 0.033 M, [$CuCl_2$] = 2.7 M, [LiCl] = 3.3 M. [b] Relative yield estimated from the intensities of the rotational transitions in the microwave spectrum. For the present semiquantitative purpose the concentration ratio of the different species was assumed to be given, with sufficient accuracy, by the intensity ratio of the corresponding spectral lines (cf. Table II), corrected by the square ratio of the corresponding frequencies. [c] Only *threo*-**3** (>90%) could be detected in the microwave spectrum. [d] Only *erythro*-**3** (>90%) could be detected.

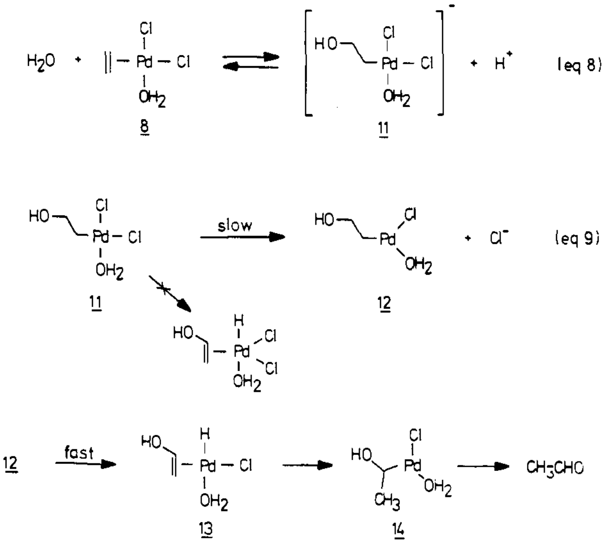


mechanism deprotonation of coordinated water in complex **8** accounts for the acid inhibition (eq 6, Scheme III). The rate-determining step is pictured as the formation of σ complex **10**, by cis addition of coordinated hydroxyl and palladium to ethene. Hydride shift in the σ complex **10** and formation of palladium(0) would then give acetaldehyde. Other possibilities for the reaction **8** → acetaldehyde are discussed below. The assumption that the hydroxypalladation step is the rate-determining step was based on the low isotope effect observed[11] for ethene-d_4 (k_H/k_D = 1.07). It was argued[4a,11,26] that, if the rate-determining step occurred after the hydroxylation, the hydride shift would mix into the rate expression and a considerable isotope effect would be observed. An alternative reaction path, which involves rate-determining attack of hydroxyl on the neutral π complex **8**, is also possible in principle from the rate expression. However, when reasonable values for the equilibrium constants for eq 4 and 5 are inserted[4a,11] into the rate expression, the hydroxylation step becomes faster than the rate of a diffusion-controlled process in solution, which is impossible.[11]

Scheme III

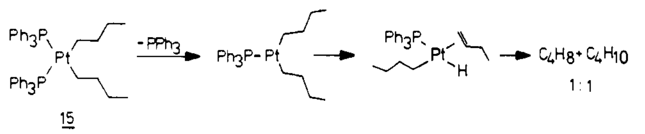


Scheme IV



Although the trans stereochemistry found here for the hydroxypalladation step has been determined at a higher chloride ion concentration (≃3 M)[27] than the one used in the kinetic studies (up to ≃1 M),[11,12] it is very unlikely that a lower chloride ion concentration would change the steric course of the reaction. Thus the stereochemistry found here for the hydroxylation appears to be at variance with kinetic data.[7b,11] However, modification of the mechanism proposed earlier, in which Scheme III is replaced by Scheme IV, renders external attack by water consistent with the kinetic data. In this modified mechanism (Scheme IV) we suggest that the hydroxylation takes place in a reversible reaction by external attack of water on **8** (eq 8), followed by a rate-determining step in which loss of chloride from the σ complex **11** takes place. Equation 8 then accounts for the acid inhibition. A reversible hydroxypalladation-deoxypalladation reaction is likely since the addition step in other related reactions, such as oxymercuration and to some extent aminopalladation, is reversible.[28,29] The dissociation of a chloride ligand from **11** would give a 14-electron complex **12**, which should be prone to undergo rapid β-elimination to give **13**. This would be consistent with the fact that essentially no isotope effect is found[11a] for ethene-d_4, the rate-determining step occurring before the β-elimination. Readdition[13,25] of palladium hydride to coordinated vinyl alcohol to give **14**, followed by β-elimination over carbon and oxygen, would give acetaldehyde and palladium hydride.

The 16-electron complex **11** could in principle undergo β-elimination to give **13** via a five-coordinated 18-electron complex. This path, however, would result in a considerable isotope effect, which is inconsistent with experimental data.[4,26] Furthermore, the idea that β-elimination is favored in a 14-electron three-coordinated complex is supported by recent work on nickel[30] and platinum[31,32] complexes. Grubbs et al.[30] found that loss of phosphine from the diphosphine complex of nickelocyclopentane to the three-coordinated monophosphine complex was necessary for β-elimination to take place. Whitesides et al.[31] observed that the rate-determining step for the decomposition of **15** was dissociation of a phosphine ligand, before β-elimination occurred (eq 10). This provides good support for the sequence **11** → **12** → **13** depicted in Scheme IV.



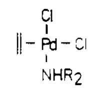
15

(eq 10)

Dissociation of a chloride ligand as the rate-determining step also explains the stabilizing effect of chloride. At low chloride concentrations the σ complex is rapidly decomposed to aldehyde, whereas, at high chloride concentrations, its decomposition to aldehyde is depressed and it is stable enough to be trapped by oxidative cleavage.

It is interesting to compare the Wacker hydroxylation with the palladium promoted amination of monoolefins,[10,33] since both reactions are trans-addition processes[10a] and display several similarities. Thus, in both reactions, cis olefins react more slowly than trans olefins,[10,34] in contrast to what is generally found for related trans-addition reactions such as methoxypalladation,[8a] oxymercuration,[28] and aminomercuration.[35] This was initially believed[33] to reflect a cycloaddition character, but is more likely an effect[10b] of the combination of a "product-like" transition state and a stronger π-olefin-metal complex for cis olefins than for trans olefins.

At temperatures above 0 °C the addition step in the amination reaction has been shown[29b] to be reversible. Thus, both the hydroxypalladation and the aminopalladation appear to be reversible, which is in accordance with the reported[36] reversible addition of pyridine to a platinum olefin complex. Furthermore, the complexes **16** and **17** are probable intermediates in the amination reaction. In these complexes, as in the crucial intermediate **8**, in the Wacker hydroxylation, the nucleophile is coordinated to the metal prior to the reaction of the olefin. Despite this, the mode of reaction is *external* attack of another molecule of the nucleophile. This shows that external trans attack is strongly favored over intramolecular cis attack in these cases. The former mode of attack is also found for related nucleophiles like acetate, alcohols, etc. In contrast, another type of nucleophiles, like aryl, alkyl, and hydride, prefer the intramolecular mode of attack and are transferred from the metal to carbon. A similar correlation between steric course of the reaction and type of nucleophile utilized is also found for π-allyl-[37-39] and σ-alkylpalladium[6,40-44] systems. A general model for nucleophilic attack on π-olefin-, π-allyl-, and σ-alkylpalladium complexes is emerging (Scheme V). This model should also be valid for other analogous 16-electron transition metal complexes, Nucleophiles like acetate, alcohol, amine, water, malonate, etc., prefer to attack externally (path A, S_N2-type attack) even if a molecule of the nucleophile is coordinated to the metal, whereas nucleophiles like aryl, alkyl, and hydride are transferred from the metal to carbon (path B insertion, reductive coupling). Certain nucleophiles, such as halide, fall in between and may add in both manners (path A or B) depending on the concentration of free nucleophile in solution.[4a,7b,16,41]

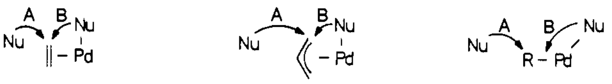


16

17

The transformation of the σ complex **11** into acetaldehyde and palladium(0) (or palladium hydride) is an interesting reaction that bears some relation to some of the transformations catalyzed by vitamin B_{12} and related cobalt complexes.[45] Experiments on ethene oxidation with palladium(II) in D_2O showed that the acetaldehyde formed contained no deuterium,[4,46] which excludes a path via free vinyl alcohol in solution. If β-elimination occurs, the vinyl alcohol formed must therefore remain coordinated, so that the hydride can readd. A β-elimination–readdition sequence was first proposed by Jira et al. in 1966.[47] However, these authors suggested the rate-determining step to be the decomposition of a α-hydroxyethylpalladium complex (related to **14**) to acetaldehyde. In this mechanism the rate of the overall hydride shift (β-elimination–readdition) will appear in the rate expression. It was argued that the isotope effect in the equilibrium reactions for elimination and readdition would cancel, resulting in a low net isotope effect, which would agree with the low isotope effect observed ($k_H/k_D = 1.07$). However, it has later been shown[26] that 1,2-dideuterioethene gave CH_2DCDO-CHD_2CHO in a ratio of ≃1.7–1.8 (1.7,[26a] 1.86[26b]) indicating that there is a net isotope effect in the hydride shift. This isotope effect is not observed in the overall reaction rate,[4] and therefore the rate-determining step must take place before the hydride shift.

Scheme V



Nu_A= CH_3COO^-,[7] CH_3OH,[8,9] R_2NH,[10] H_2O (this work)

Nu_B= aryl,[7b] alkyl,[7b] hydride[4]

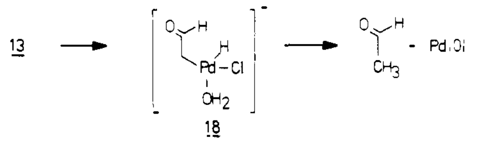
Nu_A= R_2NH,[37] $^-CH(COOR)_2$[38]

Nu_B= aryl[39]

Nu_A= CH_3COO^-,[6a,40] CH_3OH,[41] R_2NH,[6b] H_2O[42]

Nu_B= alkyl,[43] hydride[44]

Other possible routes for the transformation of σ complex to acetaldehyde are the concerted hydride shift proposed by Henry[11] and the deprotonation of the coordinated vinyl alcohol in **13** and formation of the β-oxoalkylpalladium complex **18**. Reductive elimination of hydride and the alkyl group in **18** would produce acetaldehyde (eq 11). The analogous conversion of a vinyl alcohol platinum complex into a β-oxoalkylplatinum complex has in fact been observed.[48]



(eq 11)

After the publication of our preliminary report[14] on this work, others[49] have also come to the conclusion that the hydroxypalladation of monoolefins is a trans process. The formation of (*Z*)-α,β-dideuterio-β-propiolactone from the palladium(II) catalyzed oxidation of (*E*)-**2** in the presence of carbon monoxide is consistent with a trans-hydroxypalladation step followed by insertion of carbon monoxide (with retention) and ring closure.

Concluding Remarks

The modified mechanism proposed in this paper (Scheme IV) for the palladium(II) catalyzed oxidation of ethene (the Wacker process) is compatible with all data known for the reaction, including kinetic data,[4,11,12] isotope effects,[11a,26] and the stereochemistry[14] of the hydroxypalladation step (this work). The present data do not entirely rule out other conceivable pathways. First, nucleophilic attack by water on the negatively charged π-olefin complex **9** is also consistent with the kinetic data. However, it is very unlikely, as also noted by Henry,[4a] that nucleophilic attack would occur on a negatively charged π-olefin-metal complex.[50] Second, it might be argued that the high chloride concentration used in our study would hinder coordination of water and thus inhibit[4a,51] a competing cis attack. Here too, however, nucleophilic attack by water would have to occur on a negatively charged complex (**7**), which is highly unlikely.[4a,50] Finally, the present data do not exclude the alternative process for **13** → acetaldehyde (eq 11), but the process via **14** and β-elimination over oxygen (Scheme

IV) seems more likely. In fact, recent work[52] indicates that aldehyde formation is very rapid from a manganese complex related to **14.**

It is interesting to note that a rate expression, identical with that of the Wacker hydroxylation (eq 3), has recently been determined[53] for the oxidation of ethene by palladium(II) chloride in methanol. The authors suggested a rate-determining cis-methoxypalladation, on the basis of the same arguments as used for the oxidation in water.[4a,7b,11] However, we would like to note that, with an alternative interpretation (cf. this work) of the kinetic data, a mechanism similar to that proposed in Scheme IV would apply also to this reaction. Present knowledge about the methoxylation does not entirely admit such a conclusion, since trans-methoxypalladation has only been shown[8,9] in cases where ligands such as carbon monoxide or cyclopentadienyl and phosphine are coordinated to palladium. These ligands probably prevent coordination of methanol to the metal and one cannot entirely exclude that they might inhibit[4a,51,53] a competing cis attack. Studies on the stereochemistry of methoxypalladation in the absence of strong coordinating ligands therefore seem desirable.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. NMR spectra were obtained with a Varian EM 360 spectrometer. Microwave spectra were obtained with a Hewlett-Packard Model 8460 A microwave spectrometer equipped with Stark modulation at 33.33 kHz. GLC analyses were performed on a 6 ft × $^1/_8$ in. (i.d.) column packed with 5% Carbowax 20M (100-120 mesh).

(*E*)- and (*Z*)-1,2-dideuterioethenes (**2**) were prepared[54] by reduction of dideuterioacetylene and showed bands in the IR spectrum at 987 and 843 cm^{-1}, respectively. (*E*)- and (*Z*)-1,2-dideuterioethene oxides (**4**) were prepared[19] by hypobromous acid addition to the corresponding ethene-d_2, followed by treatment of the bromohydrin produced by hydroxide ion.

Preparation of Authentic Chloroethanols-d_2. *erythro*-1,2-Dideuterio-2-chloroethanol (*erythro*-3). To a well-stirred solution of sodium hypochlorite (15 mL, 8-12% active chlorine) at 0 °C, were added simultaneously gaseous (*E*)-1,2-dideuterioethene and 2 M HCl (12 mL) over a period of 1 h; 240 mL of ethene-d_2 was consumed. Another 3 mL of the sodium hypochlorite solution was added dropwise during 15 min under simultaneous addition of ethene-d_2. This resulted in another 100-mL consumption of ethene-d_2. After the second addition was complete, the solution was stirred for 2 h. The aqueous phase was extracted once with 3 mL of ether in order to remove 1,2-dichloroethane. Then the aqueous phase was saturated with NaCl and extracted with ether (4 × 15 mL). The ether phase was dried ($MgSO_4$) and concentrated. Distillation of the residue gave a pure sample of *erythro*-**3**. For the microwave spectrum see Table I.

threo-**3** was prepared by the same procedure from (*Z*)-1,2-dideuterioethene. For the microwave spectrum see Table I.

***erythro*-1,2-Dideuterio-2-hydroxyethylmercuric Chloride (5).** Following the procedure by Hoffmann and Sand,[55] gaseous (*E*)-**2** and 0.75 M KOH (25 mL) were added slowly and simultaneously to a stirred solution of $Hg(NO_3)_2$ (2.25 g, 6.9 mmol) and acetic acid (0.7 mL) in water (45 mL). When the addition was complete the pH was ~11. NaCl (0.41 g, 7 mmol) was added and the clear solution was treated with CO_2 at 0 °C. The white precipitate was collected. Concentration of the aqueous solution gave more precipitate: yield 1.43 g (74%); mp 153-155 °C (methanol) (lit.[55] mp 155 °C); NMR (Me_2SO-d_6) δ 3.64 (br d, J = 8.4 Hz, 1, CH-OH), 1.87 (br d, 1, CH-Hg).

$PdCl_2$-$CuCl_2$-LiCl Solution. A solution in water with the following concentrations was used: $[PdCl_2] = 0.033$, $[CuCl_2] = 2.7$, $[LiCl] = 3.3$ M.

Oxidation of (*E*)-2 with the $PdCl_2$-$CuCl_2$-LiCl Systems. The $PdCl_2$-$CuCl_2$-LiCl solution (20 mL) was introduced into a 90-mL glass autoclave which had been cooled with liquid nitrogen. The autoclave was evacuated and 500-600 mL of (*E*)-**2** was condensed into the system. The autoclave was closed and allowed to reach room temperature. This gave a gauche pressure of ~5 kg/cm^2. The reaction mixture was stirred for 20-40 h at 20 °C, and during that time the gauche pressure slowly decreased. The reaction mixture was extracted with ether (5 × 10 mL). The ether phase was washed with brine (2 × 5 mL), dried ($MgSO_4$), and concentrated. Yield, as shown by GLC, varied from 70 to 100 mg. Distillation of the crude chloroethanol-d_2 gave a sample that was analyzed by microwave spectroscopy. The results are given in Table III.

Conversion of Chloroethanol-d_2 to Ethene-d_2 Oxide. The crude chloroethanol-d_2 obtained above from the palladium catalyzed reaction of ethene-d_2 was treated with 6 M NaOH (0.3 mL) under reduced pressure. The ethene-d_2 oxide evolved was collected in a liquid nitrogen trap. The epoxide was analyzed by microwave spectroscopy. The results are given in Table III.

Reaction of 5 with the $PdCl_2$-$CuCl_2$-LiCl System. To the aqueous $PdCl_2$-$CuCl_2$-LiCl solution (13 mL) was added **5** (281 mg, 1 mmol) in 10 portions during 15 min. The mixture was stirred at room temperature for another 45 min. The gas evolved was collected and shown by IR analysis to be (*E*)-1,2-dideuterioethene (>90% (*E*), ν 987 cm^{-1}).

Extraction of the reaction mixture with ether (4 × 10 mL) and GLC analysis indicated a chloroethanol yield of 40%, based on the mercury compound. The ether phase was dried ($MgSO_4$) and concentrated to give a sample of crude **3**, which was transformed into the epoxide as described above. Microwave analyses of the ethene-d_2 oxide showed that the ratio of Z:E to be 96.1:3.9.

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The Triplet State of the Chlorophyll Dimer[1]

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Abstract: The photoexcited triplet state properties of chlorophyll aggregate systems in vitro were investigated by zero-field optically detected magnetic resonance (ODMR) spectroscopy at 2 K. Measurements of the triplet state zero-field splittings, overall triplet lifetimes, and individual spin sublevel intersystem crossing rate constants were obtained for solutions of chlorophyll *a* and zinc-substituted chlorophyll *a* and for the covalently linked dimeric derivative of pyrochlorophyllide *a*. The triplet-state properties found for these systems are interpreted within the framework of the triplet exciton model to assess the applicability of the exciton approach in determining the geometry of chlorophyll aggregate systems and to evaluate structural features of chlorophyll systems proposed as models for in vivo chlorophyll.

I. Introduction

It has been recognized for some time that the chlorophyll molecule is uniquely suited for forming aggregate structures utilizing its magnesium metal center and carbonyl ring substituents. Such structures form the basis for most of the present models of the pigment complexes proposed for in vivo chlorophyll units in photosynthesis.[2-7] Recent work using both optical spectroscopy[8] and magnetic resonance[9,10] has shown that the reaction center in photosynthetic systems contains a pair of strongly interacting chlorophyll molecules, the so-called "special pair", which is involved in the initial photophysical processes of the reaction center.[2] Models for the geometry of such a reaction center dimer have been proposed by Fong[5] and by Katz and co-workers.[2,6] All the models considered for the reaction center structures of photosynthetic systems involve water-linked chlorophyll (or bacteriochlorophyll) dimers. Fong and his group first suggested that the chlorophyll dimer in the reaction center is held together by two water molecules coordinated and hydrogen bonded to provide a plane-parallel dimer structure with C_2 symmetry.[5] In his most recent work Fong postulates that such dimers may be formed from either the chlorophyll monohydrate (Chla·H$_2$O)$_2$ or the dihydrate (CHla·2H$_2$O)$_2$, which have been proposed respectively to be the P700 and water-splitting reaction centers in plant photosynthesis.[7,11] The two dimer structures differ in that the C10 ester carbonyl group is used for hydrogen bonding by the Mg-coordinated water molecule of the chlorophyll monohydrate, whereas in the chlorophyll dihydrate the C9 keto carbonyl unit is utilized.[7,11] Katz and co-workers also proposed a reaction center dimer containing one water molecule linking two plane-parallel chlorophylls (although this model does allow for freedom of motion away from the plane-parallel configuration).[2] In their most recent work, however, they also invoke a dimer locked into a plane-parallel arrangement by two water molecules coordinated to the central Mg atoms, but hydrogen bonded to the chlorin rings by the C9 keto carbonyl group.[6] Further, the Katz group proposes a structure for the antenna system requiring no water linkages but, rather, utilizing self-coordination among chlorophylls, with one chlorophyll acting as a donor via its carbonyl substituents to the Mg atom of another.[2] The carbonyl–Mg self-aggregation can lead to the formation of large networks (oligomers) of chlorophylls making up the antenna system.[2]

In the present paper we explore the use of the triplet state as a paramagnetic probe into the structural features of chlorophyll complexes, essentially using the triplet state of chlorophyll as a particularly convenient "spin label",[12,14,15] one which can be introduced nondestructively into the system of interest by photoexcitation.

The triplet state of the chlorophyll molecule has been studied

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