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Photolysis of Zeise salt in aqueous solution
Photocatalysis of the hydration of olefins to alcohols

Horst Kunkely, Arnd Vogler *

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

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ABSTRACT

The photolysis of aqueous Zeise salt essentially leads to the release of ethylene, but about 10% undergo a photohydration which is initiated by MLCT excitation:

$$Pt^{II}Cl_3(C_2H_4)]^- + 2H_2O \xrightarrow{h\nu} [Pt^{II}(H_2O)Cl_3]^- + CH_3CH_2OH$$

Since $[Pt(H_2O)Cl_3]^-$ adds again ethylene to regenerate $[Pt(C_2H_4)Cl_3]^-$ the overall reaction proceeds as a photocatalysis converting C_2H_4 to C_2H_5OH. When ethylene was replaced by 1-hexene the photoaquation to 1-hexanol takes place with $TON > 2.30$.

The hydration of ethylene to ethanol is a very important reaction in organic chemistry

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH \tag{1}$$

It is carried out for the commercial production of ethanol in large scale and proceeds as acid catalysis, for example with phosphoric acid as catalyst at 300 ° C and a pressure of 60 to 70 atmospheres. Owing to the high activation energy [1] this hydration does not take place under ambient condition even in the presence of catalysts. We anticipated that this aquation might occur photochemically. Transition metal complexes with ethylene as ligands are good candidates for such a photoreaction. Previous studies of the photochemistry of olefin complexes [2,3] have not considered this possibility. For example, the photochemistry of Zeise salt has been examined in quite some detail by Natarajan and Adamson in 1971 [4]. The most efficient reaction was found to be the ejection of ethylene as antithermal behavior:

$$[Pt^{II}Cl_3(C_2H_4)]^- \xrightarrow{h\nu/H_2O} [Pt^{II}Cl_3(H_2O)]^- + C_2H_4 \tag{2}$$

It was assumed that this release is initiated by LF (ligand field) excited states which generally induce ligand substitutions. However, a theoretical investigation later led to the conclusion that this photolysis originates from a $Pt^{II} \rightarrow \pi^*$ ethylene MLCT excited state [5]. This suggestion, in turn, caused our suspicion that the photoejection of ethylene might not be the only reaction with the participation of the ethylene ligand. Interestingly, in the original study 8% of the released ethylene could not be recovered [4]. Now, we report our observation that ethanol is indeed formed in this photolysis which can also proceed as a rather simple photocatalysis for the conversion of olefins to the corresponding alcohols.

The photolysis of Zeise salt in aqueous solution proceeds essentially in agreement with previous observations [4]. The spectral changes which accompany the irradiation indicate the release of ethylene as a ligand. Upon addition of chloride to the photolyzed solution $PtCl_4^{2-}$ is formed from the Pt(II) complex which ejected ethylene while the starting complex $[Pt(C_2H_4)Cl_3]^-$ is not affected. Moreover, the photolysis led also to the formation of ethanol which was detected by an enzyme-based (alcohol dehydrogenase or alcohol oxidase) method provided as UV test at 340 nm (Roche) or saliva test (Sanelco), respectively. This measurement revealed that a stoichiometric ratio of $PtCl_4^{2-}$ to ethanol of 10. Accordingly, about 10% of released ethylene was converted to ethanol which was formed with a quantum yield $Ø = 0.01$ at $\lambda_{irr} = 305$ nm. The amount of 8% of the released ethylene which could not be recovered [4] roughly corresponds to the amount of ethanol formed in the photolysis.

The photochemical release of ethylene leads to the formation of $[Pt(H_2O)Cl_3]^-$ which is able to add free ethylene again as a ligand. It follows that the hydration of ethylene or other olefins should proceed as photocatalysis. We examined this assumption but used 1−hexene instead of ethylene for experimental convenience. The detection and determination of 1−hexanol is carried out and by the same procedure as the analysis of ethanol. 1−Hexene is a liquid which is not miscible with water. Upon addition of this olefin to a $PtCl_4^{2-}$ containing aqueous solution, 1−hexene forms a separate layer on the top. A slow stream of argon did not only prevent the access of oxygen but as stirring procedure this argon flow provided the saturation of this aqueous solution with 1−hexene which is then available for coordination to Pt(II). The photolysis of this solution showed that it takes place as a photocatalysis

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* Corresponding author. Tel.: + 49 941 943 4716.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

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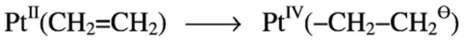


$$Pt^{II}(CH_2{=}CH_2) \longrightarrow Pt^{IV}(-CH_2-CH_2^{\ominus})$$

Scheme 1.

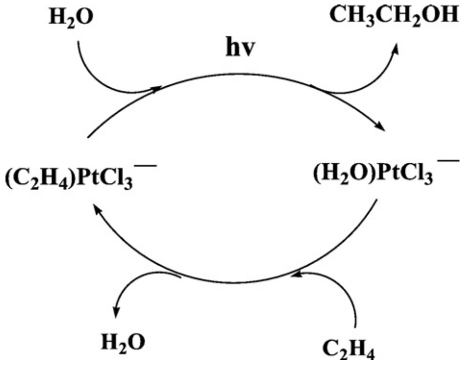
for alcohol formation. After irradiation with $\lambda = 254$ nm for 5 h the TON (1−hexanol/$PtCl_4^{2-}$) amounts to 2.30. This TON can be certainly increased by careful control of the reaction conditions but side reactions, in particular the photooxidation of Pt(II) to Pt(IV) [4] can interfere with the desired photocatalysis.

MLCT ($Pt^{II} \rightarrow \pi^*$ ethylene) excitation of $[PtCl_3(C_2H_4)]^-$ requires irradiation with light shorter than 400 nm [5]. It is associated with a shift of electron density from Pt(II) to ethylene and in a limiting description the relaxed MLCT state may be viewed as a Pt(VI) complex.

It is well known that MLCT states can lead to the release of ligands [6,7], but Scheme 1 suggests that the negative charge of the ligand facilitates also the addition of a proton and subsequently of hydroxide regenerating Pt(II) with the formation of ethanol (Scheme 2).

The overall process is then simply a hydration of ethylene to generate ethanol according to Eq. (1). In the original study [4] this mode was overlooked since it is not very efficient ($\varphi = 0.01$) in comparison to the main reaction, the release of ethylene, which takes place with $\varphi = 0.1$ at $\lambda_{irr} = 305$ nm. Nevertheless, the formation of ethanol is rather interesting not only in its own right but also because of its potential to perform this photolysis as photocatalysis.

In aqueous solution Pt^{2+} ions are well known to add olefins as a ligand. Since the photolysis of $[PtCl_3(C_2H_4)]^-$ or most likely of any other Pt(II) ethylene complex leads to the formation of some ethanol but preserves Pt(II), the ethylene complex can simply be regenerated by a sufficient supply of ethylene. The formation of ethanol proceeds then as a photocatalysis:



$$\underset{OH^-}{\overset{}{Pt^{IV}}} \!-\! CH_2 \!-\! \underset{H^+}{CH_2^{\ominus}} \longrightarrow Pt^{II} + CH_3CH_2OH$$

Scheme 2.

The competing photorelease of C_2H_4 from $[Pt^{II}Cl_3(C_2H_4)]^-$ does only reduce the efficiency of the desired photohydration of ethylene but does not interfere with its occurrence. Side reactions of the photolysis of $[Pt^{II}Cl_3(C_2H_4)]^-$ may lead to a slow loss of Pt(II) by photooxidation to Pt(IV) [4].

Owing to an easier handling of a liquid instead of a gas the photocatalysis was probed with 1−hexene which is converted to 1−hexanol upon photolysis of Pt^{2+} ions in aqueous solution. As expected the TON exceeds the minimum of 1. At an irradiation time of about 5 h the TON amounts to 2.30. The long irradiation time is apparently necessary because of the low light intensity at $\lambda_{irr} = 254$ nm. Moreover, it is probably also caused by the slow regeneration of the Pt(II) hexene complex which could originate from the small concentration of hexene in the aqueous solution owing to its low solubility.

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