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Dehydrogenation of 1,3-cyclohexadiene photocatalyzed by osmocene

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ABSTRACT

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The activation and chemical transformation of C-H bonds in alkanes continues to attract much attention [1–5]. As a basic step the oxidative addition of C-H to coordinatively unsaturated transition metal complexes plays a fundamental role. Frequently, suitable coordination compounds are initially generated in situ by the photolysis of rather stable coordination compounds. This leads to the release of ligands and produces very reactive intermediates for oxidative additions. Generally, only the generation of the active coordination compound is a photochemical process while the subsequent activation and chemical transformation of CH-bonds are thermal reactions. In this context the question arises if it is possible to activate and functionalize alkanes directly by light. Of course, direct $\sigma\sigma^{\hat{}}$ excitation of a CH-bond is conceivable but requires extremely high photon energies which are not accessible by conventional methods. In distinction, it is also feasible to transform alkanes by intermolecular photoreactions using a metal complex as a stoichiometric or catalytic reagent. Charge-transfer-to-solvent (CTTS) excitation [6,7] may serve as starting point for such considerations. Prominent examples are irreversible photooxidations of reductants such as ferrocene by halogenated alkanes including chloroform. The antibonding C–Cl σ orbitals are apparently accessible by direct CT from metal complexes. In contrast, CTTS of metal complexes in pure alkanes has not yet been observed. The C–H σ orbitals are apparently too high in energy and photoreactions of internally excited metal complexes with alkanes are also unknown. Other candidates as CT acceptors are, for example, olefins since they provide low-energy π orbitals. Photochemical reactions of olefin complexes induced by MLCT excitation are well known

Osmocene acts as a photocatalyst for the dehydrogenation of 1,3-cyclohexadiene which yields benzene and hydrogen. It is suggested that the primary photochemical step is an electron transfer from the excited osmocene to the diene.

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[7,8]. In this context, we wish to report the dehydrogenation of 1,3-cyclohexadiene (1) photocatalyzed by osmocene ($OsCp_2$).



The diolefin 1,3-cyclohexadiene (1,3-c) has been chosen for various reasons. While the π^* orbital of 1,3-c should act as CT acceptor the subsequent chemical transformation could also involve the adjacent saturated $-CH_2-CH_2-$ moiety. Osmocene is a well known reductant [9] but owing to its high stability it was expected to participate in a reversible photoinduced electron transfer. Accordingly, it would serve as a catalytic reagent. Generally, dehydrogenations of alkanes are very attractive processes for functionalization [1–4]. Since they are mostly endothermic, light may not only assist to activate the alkanes but also supply the necessary excess energy.

The direct photolysis of 1,3-c in solution is well known to lead to a ring cleavage with formation of hexatriene [10–15] in high quantum yield (ϕ = 0.4) at λ_{irr} = 254 nm [11]:



The photodehydrogenation to benzene (1) takes apparently place only in the gas phase [16,17] but has not yet been observed in solution. The photoisomerization has been suggested to lead only to hexatriene. It can be driven almost to completion before secondary

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Fig. 1. Spectral changes during the photolysis of 7.6×10^{-5} M 1,3-cyclohexadiene in *n*-hexane under argon at room temperature after 0 min (a), 1 and 3 min (b) irradiation times with $\lambda_{\rm irr}$ = 254 nm (low-pressure mercury lamp, Hanau 6 W), 1-cm cell.

photolysis takes place. The concomitant spectral changes (Fig. 1) are in agreement with this assumption. While 1,3-c shows only a broad band at $\lambda_{max} = 257$ nm ($\varepsilon = 4600 \text{ M}^{-1} \text{ cm}^{-1}$) hexatriene displays a structured absorption at $\lambda_{max} = 256$ nm ($\varepsilon = 37,600 \text{ M}^{-1} \text{ cm}^{-1}$) with further features at $\lambda_{max} = 268$ (28,500), 249 (28,700) and 238 nm (sh, 15,800) [14,18,19]. Unfortunately, benzene is characterized by a rather similar spectrum ($\lambda_{max} = 253 \text{ nm}$, $\varepsilon = 214$) with further maxima at 265, 248, 243 nm and shoulders at 268, 238 and 234 nm [20]. However, these absorptions are much less intense than those of hexatriene. Nevertheless, traces of benzene must have been formed as indicated by the appearance of the benzene fluorescence ($\lambda_{max} = 277, 269$ and 285 nm) [20] in the photolyzed solution. Hexatriene is apparently not fluorescent in solution.

At λ_{irr} > 290 nm and in the presence of 1,3-c in low concentrations (1.67×10^{-4} M) only negligible amounts of light are absorbed and small spectral changes appear after very long irradiation times $(\sim 10 \text{ h})$. When OsCp₂ is added to this solution prior to photolysis a considerable amount of light is absorbed by this complex [21] (Fig. 2). This solution is light sensitive. The irradiation is accompanied by spectral variations which are qualitatively similar to those of the direct photolysis of 1,3-c (λ_{irr} = 254 nm). However, three different features are observed when the photolysis takes place with λ_{irr} > 290 nm in the presence of osmocene. When the photolysis is complete the absorption at λ_{max} = 254 nm reaches only ca. 60% of that of the direct photolysis taking into account a constant absorption of OsCp₂. Accordingly, another photoproduct has been formed which absorbs distinctly less than hexatriene. This photoproduct is apparently benzene as indicated by its intense emission which appears from the beginning of the photolysis.

Moreover, in distinction to the direct photolysis the irradiation in the presence of $OsCp_2$ leads to the formation of a gas. Bubbles are formed which escape from the solution. This gas is H₂ according to a standard test (gas detection pump Draeger with short term tubes for hydrogen). We suggest that the sensitized photolysis yields benzene and H₂ in addition to hexatriene.

Osmocene is hardly affected by the photolysis and can be largely recovered after irradiation. Nevertheless, very long irradiation times lead to a small loss of $OsCp_2$. It seems that this is caused by traces of oxygen which are still present in the solution saturated with argon. It follows that $OsCp_2$ serves as photocatalyst for the dehydrogenation. A crude estimate yields a TON > 16.

A detailed analysis of the spectral changes (Fig. 2) shows that the ratio of hexatriene to benzene is $1:0.64 \pm 5\%$. Furthermore, volumetric determination of the gas yields a ratio of benzene to the gas of $1:0.87 \pm 10\%$ in rough agreement with the stoichiometry



Fig. 2. Spectral changes during the photolysis of a solution containing 3.2×10^{-4} M Cp₂Os and 1.67×10^{-4} M 1,3-cyclohexadiene in *n*-hexane under argon at room temperature after 0 min (a), 30 and 60 min (b) irradiation times with $\lambda_{\rm irr}$ > 290 nm (Osram HBO 200 W/2 lamp; cut-off filter Schott WG 305/2), 1-cm cell.

of Eq. (1). The quantum yield of benzene formation depends on the concentration of 1,3-c and amounts to ϕ = 7 × 10⁻³ at 6.4 × 10⁻⁴ M 1,3-c.

Our results show that OsCp₂ sensitizes the photolysis of 1,3-c according to Eq. (3):

1,3-cyclohexadiene
$$61\%$$
 hexatriene
 39% benzene + H₂ (3)

The triplet sensitized photolysis of 1,3-c has been shown to lead to the same isomerization to hexatriene as it takes place in the direct photolysis [11]. Accordingly, the hexatriene portion in Eq. (3) might be simply formed by conventional energy transfer from the LF triplet of osmocene to the $\pi\pi^*$ triplet of 1,3-c. In distinction, the photodehydrogenation must then occur by a different mechanism. Inner and outer sphere CT excitation from reducing metal centers to olefins are well known [7,8]. We suggest that in analogy to this the dehydrogenation of 1,3-c is initiated by excited state electron transfer from osmocene as donor to the diolefin as acceptor. In the first step an ion pair should be generated (4):

$$OsCp_2 + 1, 3-C_6H_8 \xrightarrow{h\nu} OsCp_2^+C_6H_8^-$$
(4)

By a subsequent hydrogen abstraction the well known hydride complex $[OsCp_2H]^+$ [22] could be formed (5):

$$OsCp_2^+C_6H_8^- \to OsCp_2H^+C_6H_7^-$$
(5)

Finally, hydride transfer from $C_6H_7^-$ to $[OsCp_2H]^+$ would lead to the product formation (6):

$$OsCp_2H^+C_6H_7^- \to OsCp_2 + H_2 + C_6H_6$$
(6)

While this is a reasonable mechanism modifications are also conceivable but there is little doubt that osmocene acts as a photocatalyst.

The CTTS transition of ferrocene appears as new absorption band when this metallocene is dissolved in halogenated alkanes [6,7]. In contrast, such a band is not observed when osmocene is dissolved 1,3-c or mixtures of 1,3-c with hexane. However, such absorptions might be very weak and escape detection. The population of CTTS states could occur by radiationless transitions from internal states of the electron donor [23,24] which is initially excited. This is equivalent to an excited state electron transfer process. In this context it should be emphasized again that dehydrogenations of alkanes and alkenes frequently proceed via oxidative addition of such organic substrates to reducing metal complexes with formation of a hydride complex as an intermediate [1–5]. The thermal [25,26] and photochemical [27] dehydrogenation of 1,3-c by metal complexes has been reported previously and also assumed to proceed by this mechanism. Common features with the dehydrogenation by osmocene can be recognized although electron transfer (Eq. (4)) as initial step seems to be an important difference. Of course, $OsCp_2$ does not provide as vacant coordination site which is required for an oxidative addition.

In summary, we describe the dehydrogenation of 1,3-cyclohexadiene to benzene photocatalyzed by osmocene. We suggest that the photoactivity is based on excited state electron transfer from $OsCp_2$ to the diolefin. Even if the dehydrogenation of this olefin is not of any practical value this photocatalysis may stimulate further studies in this area.

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