

Photooxidation of Methane to Methanol by Perrhenate in Water under Ambient Conditions

Horst Kunkely and Arnd Vogler

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

Reprint requests to Prof. Dr. Arnd Vogler. E-mail: arnd.vogler@chemie.uni-regensburg.de

Z. Naturforsch. **2013**, *68b*, 891–894 / DOI: 10.5560/ZNB.2013-3104

Received April 3, 2013

The oxidation of methane to methanol takes place selectively by the photolysis of perrhenate in aqueous solution in the presence of methane. This photoreaction is formally an oxygen atom transfer. Because the reoxidation of the reduced perrhenate is accomplished with hydrogen peroxide the overall process can be viewed as photocatalytic oxidation of methane to methanol: $\text{CH}_4 + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$.

Key words: Rhenium Complexes, Photochemistry, Methane, Catalysis

Introduction

The activation and functionalization of alkanes remains to be a field of much activity [1]. This is not only of academic interest, but practical aspects of industrial and commercial applications play an important role. In particular, the facile conversion of methane to methanol could provide a basis for the “methanol economy” [2] with novel utilizations in organic chemistry. The application of such systems for the chemical storage of solar energy and its simple manipulation and transportation is a very attractive aspect. Unfortunately, methane is characterized by a quite low reactivity owing to its high C–H bond energy which amounts to 104 kcal. Accordingly, high activation energies are required to facilitate functionalization. However, under these conditions it is difficult to control any reaction and to achieve selectivity. In particular, oxidations can frequently not be stopped when the requested product is formed, and over-oxidation may take place terminating at the thermodynamic sink, *e. g.* carbon dioxide. For that reason it is quite intriguing that Nature developed the enzyme methane-monoxygenase which accomplishes the conversion of methane to methanol under ambient conditions. Nevertheless, much progress has been achieved in this research field by the investigation of the interaction of alkanes including methane with transition metal centers as an important branch of organometallic chemistry [3–6].

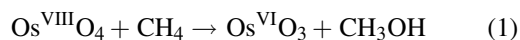
In this context it is quite surprising that photochemical studies are still rare in this area. Although irradiation has been used to generate active metal complexes [3–6] the photoconversion of alkanes themselves is largely unexplored. The light energy should not only promote photochemical reactions in general but in particular could supply the requested activation energy. Selectivity may be preserved since the photochemistry can occur under ambient conditions. These considerations initiated our present study.

The thermal oxidation of alkanes by OsO_4 in aqueous solution has been examined before [7, 8], but it proceeds only at higher temperatures, and over-oxidation can apparently not be avoided. For an initial attempt we selected this system but studied the photochemistry under ambient conditions. This investigation was also facilitated by taking into account the results of previous work with OsO_4 as an efficient photooxidant [9]. However, owing to the detrimental properties of OsO_4 it was later replaced by the isoelectronic anion ReO_4^- which promotes a rather smooth photoconversion of methane to methanol.

Results

Aqueous solutions of OsO_4 are not light-sensitive as indicated by the absence of any spectral changes upon irradiation with white light or UV light ($\lambda_{\text{irr}} = 254 \text{ nm}$). However, when methane (we used natural gas consist-

ing of 97.5 vol-% methane, 1.1 % ethane and 0.8 % nitrogen) is blown through this solution during irradiation spectral variations (Fig. 1) are observed which clearly indicate the formation of $[\text{Os}(\text{OH})_4(\text{O})_2]^{2-}$ ($\lambda_{\text{max}} = 300 \text{ nm}$, $\epsilon = 1300$; 515, 34 and 680 nm, sh, 14) [9, 10] as photoproduct according to the simple stoichiometry shown in Eq. 1.



The product OsO_3 exists in aqueous solution as $[\text{Os}(\text{OH})_4(\text{O})_2]^{2-}$. Moreover, methanol was detected by an enzyme-based method (alcohol dehydrogenase or alcohol oxidase provided as UV test 340 nm from Roche or Sanelco), but only traces of CH_3OH were found. In addition, some formaldehyde was identified (Merckoquant 1.10036.0001 and Spectroquant 1.4500.0001). The lack of methanol as product is not surprising because the thermal oxidation of methanol by OsO_4 is well known [11, 12]. It is quite interesting that $[\text{Os}(\text{OH})_4(\text{O})_2]^{2-}$ can be completely reoxidized photochemically by H_2O_2 to OsO_4 ($\lambda_{\text{irr}} = 254 \text{ nm}$) while this reaction does not take place thermally [11].

Aqueous solutions of perrhenate are also light-insensitive, but when methane is passed through this solution a photolysis takes place. The concomitant spectral changes (Fig. 2) showed a pattern which resembles that of Fig. 1. Rather weak bands in the visible region at $\lambda_{\text{max}} = 430 \text{ nm}$ and 570 nm appeared but could not be assigned. They are attributed to some kind

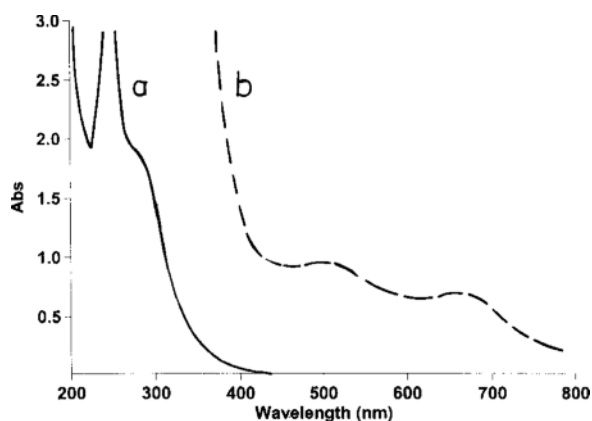


Fig. 1. Spectral changes during the photolysis of $7.6 \times 10^{-4} \text{ M OsO}_4$ in water ($\text{pH} = 9.0$) and in the presence of CH_4 (see text) after 0 min (a) and 3 h (b) irradiation time with $\lambda_{\text{irr}} = 254 \text{ nm}$ (low-pressure mercury lamp, Hanau 6 W), 1-cm cell; (b): absorbance $\times 10$.

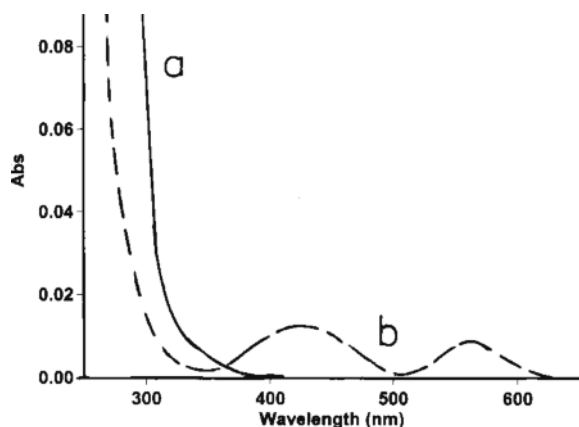


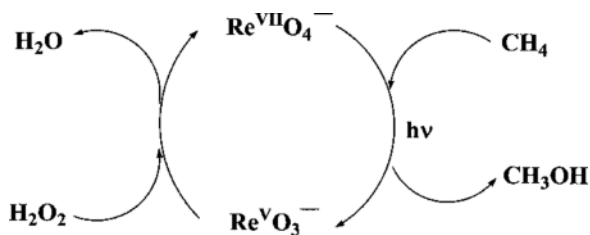
Fig. 2. Spectral changes during the photolysis of $3.6 \times 10^{-3} \text{ M NH}_4\text{ReO}_4$ in water and in the presence of CH_4 (see text) after 0 min (a) and 10 h (b) irradiation time at $\lambda_{\text{irr}} = 254 \text{ nm}$ (see Fig. 1), 1-cm cell.

of rhenate(V) such as ReO_3^- . In previous studies attempts to isolate rhenate(V) failed owing to its subsequent disproportionations [13]. However, the presence of weak bands of the photolysis products in the spectrum of Fig. 2 suggests that these originate from $d-d$ (or LF) transitions in analogy to $[\text{Os}(\text{OH})_4(\text{O})_2]^{2-}$ which is also a d^2 species. Accordingly it was assumed that the photolysis proceeds according to Eq. 2.



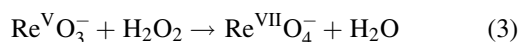
The loss of ReO_4^- was determined by measuring the decrease of the absorbance at 300 nm taking into account the residual extinction of the photolysis products at this wavelength. In addition, methanol was detected in the photolyzed solution. The reliability of this selective analysis was confirmed by control experiments with measured amounts of added methanol prior and after the photolysis. At longer irradiation times further spectral changes did not occur but only 80 % of the methane which should have been reacted according to Eq. 2 were recovered as methanol by quantitative analysis. Irrespective of the precision of this analysis ($\pm 10\%$) the loss of some methanol takes certainly place by its removal by the stream of methane passing this solution. Formaldehyde was not detected in this solution. An over-oxidation of methane is certainly not expected owing to the fact that ReO_4^- is only a weak oxidant compared to OsO_4 .

When H_2O_2 was added to the photolyzed solution of $\text{ReO}_4^-/\text{CH}_4$ the original spectrum of ReO_4^- (see Fig. 2)



Scheme 1.

was completely restored. Rhenate(V) was apparently reoxidized in a thermal reaction according to Eq. 3.



It follows that the sum of reactions 2 and 3 simply yields Eq. 4.



Discussion

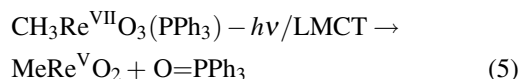
The overall reaction can be also expressed as a cyclic process which can be viewed as a photocatalytic oxidation according to Scheme 1.

The tetraoxo complexes OsO_4 and ReO_4^- are d^0 systems which have available only LMCT transitions. Both complexes can expand their coordination sphere by accepting a further ligand. However, CH_4 does not provide a free electron pair for bonding to the metal. Accordingly, complexes such as $\text{OsO}_4(\text{CH}_4)$ or $[\text{ReO}_4(\text{CH}_4)]^-$ are certainly not very stable. Moreover, the electronic interaction which could lead to a (CH_4 to metal) LMCT transition would be also very weak. As an alternative, the CT interaction of CH_4 and these tetraoxo complexes may be also of the outer-sphere (OS) CT type [14] as it is well known for OsO_4 and certain aromatic molecules [15]. Again, this type of OSCT interaction should be very weak for CH_4 as OSCT donor. Accordingly, it is not surprising that the absorption spectrum of perrhenate in water is not affected by methane passing this solution. In addition, the limited solubility of methane in water ($\sim 10^{-3}$ M) will certainly also contribute to a rather low stationary state concentration of any species containing OsO_4 or ReO_4^- and CH_4 . So it is not unexpected that the photolysis (Eqs. 1 and 2) requires a long irradiation time, also in view of the low light intensity which is available at $\lambda_{\text{irr}} = 254$ nm in our set up. Owing to the presumably very low concentration of the photoactive species, attempts to identify its absorption spectrum

were not successful. The photoactivity was restricted to the absorption of perrhenate. Accordingly, any measured quantum yield can not be attached any significance, but with regard to the light absorbed by perrhenate Φ at $\lambda_{\text{irr}} = 255$ nm it is estimated to be lower than 10^{-6} .

In terms of organometallic chemistry the photoreactivity of OsO_4/CH_4 and $\text{ReO}_4^-/\text{CH}_4$ is a further example of the significance of CT states which induce photoreactions of organometallic compounds [16]. In this context it is of interest that CH_3ReO_3 is characterized by a very reactive ($\text{CH}_3^- \rightarrow \text{Re}^{\text{VII}}$) LMCT excited state [17, 18]. The stability of the $\text{CH}_3\text{-Re}$ bond may be close to that of the $\text{H}_3\text{C-H}$ bond in methane.

A further interesting analogy should be mentioned. The photoreactions of OsO_4 and ReO_4^- with CH_4 according to Eqs. 1 and 2 can be considered as an oxygen atom transfer process. A related photolysis has been observed before (Eq. 5) [19].



The suitability of water as reaction medium may be favored by the ability of alkanes to form gas hydrates [20].

In conclusion, in aqueous solution perrhenate photooxidizes methane to methanol in a rather selective process. Because the reduced perrhenate is reoxidized by H_2O_2 the overall reaction $\text{CH}_4 + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ can be conducted as a cyclic process which represents a kind of photocatalysis.

Experimental Section

OsO_4 and NH_4ReO_4 (Puratrem) were commercially available (Strem) and used as obtained. Natural gas was provided through the pipeline of the local gas supplier. Absorption spectra were measured with a Varian Cary 50 spectrophotometer. The light sources used for irradiation were a low-pressure mercury lamp (Hanau, 6W) or a high-pressure mercury lamp (Osram HBO 200 W/2). Monochromatic light was obtained using Schott PIL/IL interference filters and Schott cutoff filters to avoid short-wavelength and second-order irradiation. In all cases the light beam was focused on a photolysis cell by a quartz lens. The photolyses were performed in 1-cm spectrophotometer cells.

Acknowledgement

We are grateful for financial support by DFG (grant Vo 211/19-1).

- [1] M. P. Doyle, K. I. Goldberg, *Acc. Chem. Res.* **2012**, *45*, 777.
- [2] G. A. Olah, A. Goepfert, G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim **2009**.
- [3] R. H. Crabtree, *J. Organomet. Chem.* **2004**, *689*, 4083–4091.
- [4] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–508.
- [5] R. G. Bergman, *Science* **1984**, *223*, 902–908.
- [6] R. H. Crabtree, *J. Chem. Soc., Dalton Trans.* **2001**, 2437–2450.
- [7] B. C. Bales, P. Brown, A. Dehestani, J. M. Mayer, *J. Am. Chem. Soc.* **2005**, *127*, 2832–2833.
- [8] J. M. Mayer, E. A. Mader, J. P. Roth, J. R. Bryant, T. Matsuo, A. Dehestani, B. C. Bales, E. J. Watson, T. Osako, K. Valliant-Saunders, W. H. Lam, D. A. Hrovat, W. T. Borden, E. R. Davidson, *J. Mol. Cat. A: Chem.* **2006**, *251*, 24–33.
- [9] H. Kunkely, A. Vogler, *Inorg. Chem. Commun.* **1998**, *1*, 7–9.
- [10] K. A. K. Lott, M. C. R. Symons, *J. Chem. Soc.* **1960**, 973–976.
- [11] T. Osako, E. J. Watson, A. Dehestani, B. C. Bales, J. M. Mayer, *Angew. Chem. Int. Ed.* **2006**, *45*, 7433–7436.
- [12] T. E. Geswindt, W. J. Gerber, H. E. Rohwer, K. R. Koch, *Dalton Trans.* **2011**, 8581–8588.
- [13] G. Rouschias, *Chem. Rev.* **1974**, *74*, 531–566.
- [14] A. Vogler, H. Kunkely, *Top. Curr. Chem.* **1990**, *158*, 3–27.
- [15] J. M. Wallis, J. K. Kochi, *J. Am. Chem. Soc.* **1988**, *110*, 8207–8223.
- [16] A. Vogler, H. Kunkely, *Coord. Chem. Rev.* **2004**, *248*, 273–278.
- [17] H. Kunkely, T. Türk, C. Teixeira, C. de Meric de Bellefon, W. A. Herrmann, A. Vogler, *Organometallics* **1991**, *10*, 2090–2092.
- [18] W. A. Herrmann, F. E. Kühn, D. A. Fiedler, M. R. Mattern, M. R. Geisberger, H. Kunkely, A. Vogler, S. Steenken, *Organometallics* **1995**, *14*, 5377–5381.
- [19] H. Kunkely, A. Vogler, *J. Organomet. Chem.* **2000**, *606*, 207–209.
- [20] C. A. Koh, *Chem. Soc. Rev.* **2002**, *31*, 157–167.