DOI: 10.1002/anie.201304768

Sandwich Complexes

Evidence for an Oxygen Anthracene Sandwich Complex**

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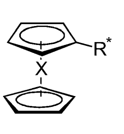
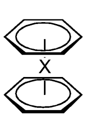
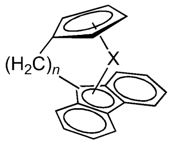
Sandwich complexes **1** and **2** have been known for many years, and their discovery was awarded with the Nobel Prize in Chemistry in 1973.[1] More recently, various chiral ferrocenes **1** were employed as asymmetric catalysts.[2] On the other hand, ansa-metallocenes of type **3** efficiently catalyze the polymerization of propylene.[3] However, oxygen sandwich complexes ($X=O_2$) were hitherto unknown, although the O=O double bond or the lone pair electrons might interact with the π-system of the arene.[4] Indeed, such π interactions play an important role in electron transfer processes,[5] and for the binding of water to aromatic residues of proteins.[6]



1 (X = Fe)

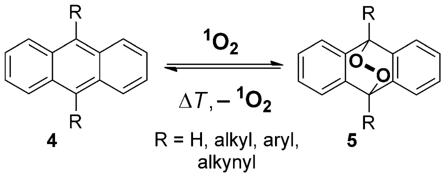


2 (X = Cr)



3 (X = $ZrCl_2$)

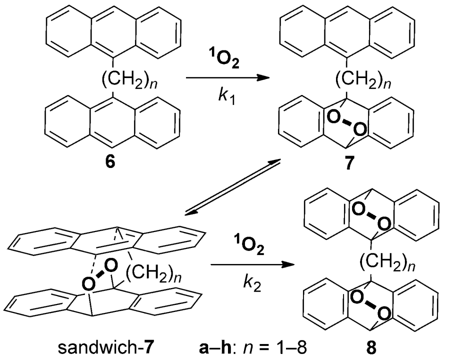
The interaction of singlet oxygen ($^1O_2$), which is the lowest excited electronic state of molecular oxygen,[7] with organic compounds is of great interest for chemistry, biology, material sciences, and medicine.[8] Furthermore, the formation of charge-transfer (CT) complexes between molecular oxygen and arenes is well established,[9] and was used for the generation of $^1O_2$ by irradiation into the CT absorption band.[10] Very recently, a pronounced effect of the local environment on the reaction rate of $^1O_2$ with tryptophan in a protein was established.[11] However, lone-pair–π interactions of endoperoxides **5** with arenes, resulting in sandwich complexes, were hitherto unknown. Such endoperoxides **5** can be easily synthesized by formal [4+2] cycloaddition of $^1O_2$ to anthracenes **4** in high yields (Scheme 1),[12] a reaction we applied in material sciences.[13]



Scheme 1. Oxidation of anthracenes **4** with $^1O_2$ to endoperoxides **5**.

Interestingly, the formation of endoperoxides **5** is completely reversible with suitable substituents (e.g. R = Ph) under thermal cleavage of oxygen, partly in its singlet state.[14] Thus, a transfer of singlet oxygen between two anthracene units might be possible. However, since the interaction of the free electron pair with another anthracene unit is expected to be very weak,[6] bis-anthryl species of ansa-type **3** seem to be more suitable substrates. Herein we describe our results on the oxidation of such acenes, giving evidence for an oxygen sandwich complex as intermediate.

Bis(anthryl)alkanes **6** are available from dihydroanthracene[15] or anthrone[16] in only two steps. We slightly improved the synthesis in terms of yields and starting materials by direct Birch reduction and alkylation of anthracene (see the Supporting Information). Thus, bis-anthryl compounds **6a–h** with chain lengths from $n=1$–8 were obtained on a gram scale. Although the intramolecular [4+4] cycloaddition of such compounds has been studied previously,[17] the reaction with $^1O_2$ was hitherto unknown. We expected two subsequent photooxygenations to mono- **7** and bis-endoperoxides **8** with different rate constants k_1 and k_2, respectively. If an oxygen sandwich complex sandwich-**7** in equilibrium with the mono-endoperoxide **7** exists, the rate of the second oxidation step should be influenced in dependence on the chain lengths *n* (Scheme 2).



Scheme 2. Photooxygenation of bis(anthryl)alkanes **6** to mono- and bis-endoperoxides **7** and **8**.

Initial experiments were conducted in chloroform, which is suitable for photooxygenations,[7,18] and anthracenes have a high solubility in this solvent.[19] $^1O_2$ was generated with tetraphenylporphin (TPP) as sensitizer by external irradiation with a sodium lamp (500 W). Owing to the wavelength of 589 nm, photochemical [4+4] cycloadditions, which take place at 366 nm, could be completely suppressed. Thus, on a preparative scale, bis-anthryls **6** (0.25 mmol, 3 mM solutions) were photooxygenated for 3–6 min; after this time thin-layer

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[**] We thank the University of Potsdam for generous financial support and Dr. Fudickar for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304768.

chromatography showed about 60–80% conversion and formation of mono- **7** and bis-endoperoxides **8**, which were isolated by column chromatography in pure form (see the Supporting Information). Complete conversion could be achieved by irradiation for more than 40 min, affording the bis-endoperoxides **8** as sole products in more than 97% yield.

For kinetic measurements, we prepared highly diluted solutions of bis-anthryls **6** in chloroform (5.0×10^{-5} M) to avoid *intermolecular* interactions of endoperoxides with unreacted anthracenes and to establish the *intramolecular* formation of an oxygen sandwich complex sandwich-**7**. Under such conditions, the photooxygenations simplify to pseudo first-order kinetics,[18] and k_1 and k_2 can be easily determined (see the Supporting Information). Furthermore, the same value for k_2 was obtained by one-step photooxygenations of the pure mono-endoperoxides **7**, isolated from the preparative scale reactions. Additionally, we measured k_1 and k_2 in competition kinetics with 9-methyl- and 9-*n*-butylanthracene as internal standards, and compared the data with previously reported bimolecular rate constants.[20] Thus, effects of $^1O_2$ concentration or quenching by the solvent could be completely ruled out. For all kinetics measurements, HPLC was the method of choice, as all of the compounds can be easily separated and detected by their characteristic retention times and UV absorptions (see the Supporting Information). The standard deviations from the mean value for repetitive measurements were very low ($\sigma < 1.4\%$) and the normalized bimolecular rate constants k_1 and k_2 with respect to chain lengths n are summarized in Table 1.

Table 1: Kinetic data for photooxygenations and [4+4] cycloadditions of bis(anthryl)alkanes **6**.

Entry	Anthracene	n	Chloroform			Acetonitrile		
			k_1[a]	k_2[a]	k_3[b]	k_1[a]	k_2[a]	k_3[b]
1	9-Methyl	–	8.10[20]	–	–	6.98	–	–
2	9-*n*-Butyl	–	5.16	–	–	4.78	–	–
3	**6a**	1	2.16	2.34	4.51	1.33	2.61	3.58
4	**6b**	2	3.88	4.46	**9.24**	2.73	2.32	**11.53**
5	**6c**	3	7.60	6.36	1.88	6.26	3.05	6.26
6	**6d**	4	7.44	9.43	1.58	6.78	**5.85**	4.91
7	**6e**	5	7.44	9.94	0.51	7.56	3.19	0.06
8	**6f**	6	7.42	10.42	0.45	7.38	3.27	0.09
9	**6g**	7	7.25	11.41	0.46	7.15	3.33	0.08
10	**6h**	8	7.05	12.20	0.48	6.97	3.63	0.09

[a] Bimolecular rate constants k_1 and k_2 (10^6 L mol^{-1} s^{-1}) for photooxygenations, determined by HPLC measurements. The standard deviations from the mean value for repetitive measurements were very low ($\sigma < 1.4\%$). [b] Unimolecular rate constants k_3 (10^7 s^{-1}) for intramolecular [4+4] cycloadditions by irradiation at 366 nm, determined by UV measurement from the decay of **6**.

For bis(anthryl)alkanes **6a** and **6b** with short chain lengths ($n = 1$–2), both rate constants k_1 and k_2 are small (entries 3 and 4), which can be explained by steric hindrance between the two anthracene moieties. The importance of steric interactions becomes evident with 9-*n*-butyl-anthracene, which reacts considerably slower than 9-methyl-anthracene (entries 1 and 2). With longer chain lengths ($n = 3$–8), steric hindrance is more and more minimized and thus the oxidation rates slightly increase (k_2) or are almost constant (k_1) (entries 5–10). The reason for this almost constant rate (k_1) might be due to intramolecular interactions of the two anthracene rings even for longer chain lengths n. Therefore, we compared the photooxygenations of bis(anthryl)alkanes **6** with their intramolecular [4+4] cycloadditions. The kinetics were measured by irradiation of highly diluted chloroform solutions of compounds **6a–h** at 366 nm under exclusion of oxygen (see the Supporting Information and Table 1). Now the unimolecular rate constants k_3 have a maximum for $n = 2$ (entry 4), in good agreement with data obtained in methylcyclohexane[17] or ethanol.[21] This can be explained by the proper chain length for the best overlap of the two anthracene rings, resulting in a fast cyclization and products with less ring strain. However, we observed some cyclization even for the homologues **6e–h** ($n = 5$–8), indicating that π–π stacking is still operative, resulting in smaller k_1 compared to k_2 (entries 7–10).

The reason that we found no evidence for an oxygen sandwich complex sandwich-**7** in our initial experiments might be due to the solvent. As the solubility of anthracenes in chloroform is very high,[19] the aromatic rings are surrounded by the solvent even stabilizing a π–π complex in a solvent cage. Thus, the expected interaction of the lone pair electrons of the mono-endoperoxide **7** with the π system[4] is too weak to replace the chloroform. Therefore, we repeated all measurements with internal standards in acetonitrile, which is suitable for photooxygenations but a bad solvent for anthracenes[19] (see the Supporting Information and Table 1). Again, the [4+4] cycloaddition was fastest with bis(anthryl)ethane **6b** ($n = 2$, entry 4). However, in contrast to chloroform, the higher homologues **6e–h** ($n = 5$–8) undergo cyclization much slower if at all (entries 7–10), indicating that π–π stacking is no longer operative and both anthracene rings can react independently with $^1O_2$. This is further supported by the faster formation of mono- compared to bis-endoperoxides ($k_1 > k_2$) owing to a statistic factor.

Most importantly, the second oxidation step (k_2) shows a remarkable maximum for $n = 4$ (entry 6). The rate of this reaction with $^1O_2$ is almost twice of all other oxidations of mono-endoperoxides **7**. This gives considerable evidence for an oxygen sandwich complex sandwich-**7d** as intermediate during the photooxygenation. Owing to the favorable interaction of the oxygen lone pairs of the endoperoxide with the π system, the electron density of the anthracene and thus the HOMO energy is increased. The importance of the local environment on the reaction rate of $^1O_2$ has been established in tryptophan oxidations very recently as well.[11] Although this effect through space is much weaker than with directly linked or remote functional groups, electron donors increase the photooxygenation rates of anthracenes in general.[18,22] The chain length of $n = 4$ fits well with the proposed ansa-structure sandwich-**7d** (Scheme 2), as owing to the two oxygen atoms the distance between the anthracene moieties has to be larger compared to the intramolecular [4+4] cycloaddition, which is favored for $n=2$ (Table 1).

To further support the formation of an oxygen sandwich complex for a defined chain length of $n=4$, we performed quantum chemical calculations using B3LYP/6-31+G** with empirical dispersion (GD2; see the Supporting Information). Thus, we started from the same geometry of mono-endoperoxides **7c–e** ($n=3$–5) and calculated three different local minima (Figure 1). Indeed, only for $n=4$ a preferred sandwich structure **7d** was found with a suitable oxygen–anthracene distance of 3.2 Å. The other homologues **7c** and **7e** gave minima with no lone-pair–π interaction.

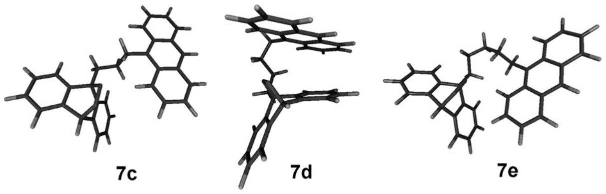

Figure 1. Calculated preferred geometries of mono-endoperoxides **7c–e** (B3LYP/6-31+G**).

The kinetic data in Table 1 have to be corrected by statistic factors of the reactive sides, from which $^1O_2$ can attack the arenes. Thus, the internal standard 9-methylanthracene and the mono-endoperoxides **7** can react from two sides, whereas the bis(anthryl)alkanes **6** have four options to be oxidized. Therefore, for comparison of the reactivity of a single anthracene moiety, the measured rate constants k_1 have to be halved compared to k_2. This calculation is not suitable for chloroform as solvent, since both anthracenes interact by π–π stacking, reducing possible reactive sides, resulting in smaller k_1. However, the kinetics in acetonitrile fit well to this model (Figure 2), showing clearly that mono-endoperoxide **7d** reacts fastest with $^1O_2$, owing to a lone-pair–π interaction. This is even more remarkable, as one side of the anthracene is blocked by the endoperoxide in complex sandwich-**7d**, and the normalized rate constant k_2 would be even higher. Another explanation might be the reversible binding of $^1O_2$ to anthracenes.[14] Thus, in complex sandwich-**7d** the oxygen might be transferred from the endoperoxide to the anthracene or stick exactly in the middle of the two acene moieties, resulting in equal binding to both anthracenes, typical for sandwich complexes. This would allow the accelerated attack of $^1O_2$ from both outer planes.

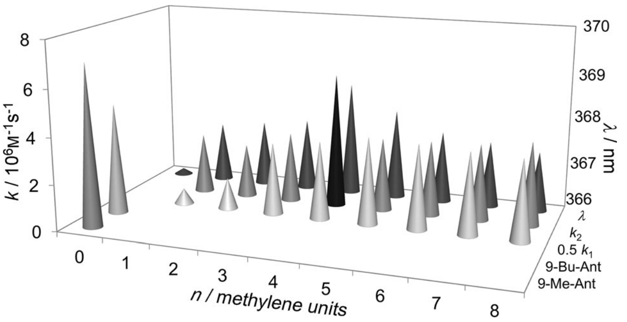

Figure 2. Corrected kinetic data of the photooxygenations of bis(anthryl)alkanes **6** and UV/Vis absorption maxima (λ_{max}) of mono-endoperoxides **7** in acetonitrile.

Finally, in an oxygen sandwich complex sandwich-**7d** the UV absorption of the remaining anthracene ring should be influenced by the lone-pair–π interaction or even show a CT absorption band. Directly linked or remote electron donors at anthracenes result in absorptions at higher wavelengths (bathochromic shift).[22,23] Therefore, we measured UV/Vis spectra of all mono-endoperoxides **7a–h** in acetonitrile (see the Supporting Information). Indeed, the largest bathochromic shift was observed again for mono-endoperoxide **7d** ($n=4$, Figure 2). Unfortunately this effect is small owing to the interaction through space and an equilibrium with the open form **7d**. To minimize possible rotations, we repeated the UV/Vis measurement of mono-endoperoxide **7d** at −45 °C, almost the freezing point of acetonitrile. Now the UV/Vis spectrum shows even a charge transfer (CT) absorption band, which is typical for oxygen–π interactions (Figure 3).[10b] In comparison, mono-endoperoxides **7c** and **7e** show at the same temperature no CT band at all (see the Supporting Information), indicating again the importance of the defined chain length of $n=4$ for a lone-pair–π interaction. All together, these spectroscopic data in combination with the kinetic measurements and the calculations give considerable evidence for the existence of an oxygen sandwich complex.

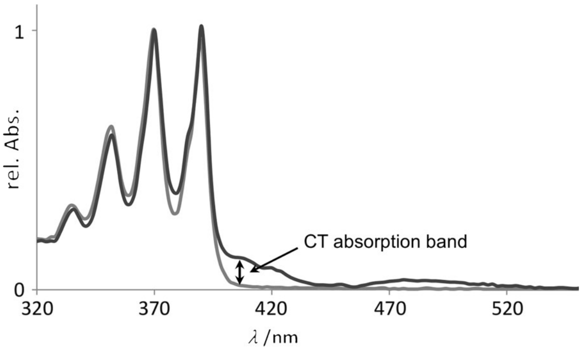

Figure 3. UV/Vis spectra of mono-endoperoxide **7d** in acetonitrile at 25 °C (gray) and −45 °C (black).

In summary, we found evidence for an oxygen sandwich complex during the photooxygenation of bis(anthryl)alkanes. Our kinetic studies showed a rate acceleration of the second oxidation step only for a chain length of $n=4$ in acetonitrile, whereas intramolecular [4+4] cycloadditions were fastest with $n=2$. This fits well with the distance of the two anthracene moieties for a sandwich complex or a direct cyclization, respectively. We supported our kinetic studies with quantum chemical calculations. Thus, a local minimum for a sandwich complex was only found for $n=4$, with a suitable oxygen–anthracene distance of 3.2 Å. As no evidence for such a sandwich complex was found in chloroform, the stabilization by oxygen lone-pair–π interactions is only moderate but substantial. Finally, further proof for an oxygen sandwich complex was found by the bathochromic shift of the UV/Vis absorption for only one mono-endoperoxide ($n=4$), with an additional CT absorption band at low temperature. Overall, the kinetic and spectroscopic data in combination with calculations give considerable evidence for the existence of an oxygen sandwich complex. Since reactions of singlet oxygen with organic compounds are important in biological processes, for the degradation of organic electronics, or medical applications, our studies should be interesting for the understanding of oxygen–acene or lone-pair–π interactions in general.

Experimental Section

Bis(anthryl)alkanes **6** were synthesized by Birch reduction of anthracene, alkylation, and subsequent oxidation with DDQ. Preparative photooxygenations were conducted on a 0.25 mmol scale in chloroform with TPP as sensitizer and external irradiation with a sodium lamp (500 W). The yields of mono- **7** and bis-endoperoxides **8** can be controlled by the reaction times. Detailed procedures for photooxygenations and [4+4] cycloadditions, analytical data, kinetic equations and evaluations, calculations, UV/Vis spectra, and HPLC chromatograms are available as Supporting Information.

Received: June 3, 2013

Keywords: arenes · peroxides · sandwich complexes · singlet oxygen · π interactions

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