High Turnover Numbers for the Catalytic Selective Epoxidation of Alkenes with 1 atm of Molecular Oxygen[**]

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Catalytic epoxidation of alkenes has attracted much attention both in industrial processes and in organic syntheses, because epoxides are among the most useful synthetic intermediates. Epoxidation of alkenes can be carried out by various techniques with various oxidants. However, stoichiometric (noncatalytic) epoxidation is still widely used, and large amounts of byproducts, particularly salts, are formed. For example, propylene oxide has been produced commercially by alkaline dehydrochlorination of propylene chlorohydrin with formation of large amounts of metal salts.[1–3] The utilization of molecular oxygen for a catalytic epoxidation without reducing reagents or radical initiators is a rewarding goal, because molecular oxygen has the highest content of active oxygen, and no byproducts are formed from it, in contrast to various other oxidants.[4–13] However, only a few ideal homogeneous epoxidations of alkenes with molecular oxygen at 1 atm without reducing reagents or radical initiators have been achieved, because organic ligands of the catalysts are degraded or the catalysts act as stoichiometric oxidants.

Therefore, a high catalyst turnover number (TON) is a key. The catalytic activity of polyoxometalates has attracted much attention, because their acidic and redox properties can be controlled at the atomic or molecular level. The strong acidity and oxidizing power of polyoxometalates have led to many studies on homogeneous and heterogeneous catalysis.[13–16] The additional attractive and technologically significant aspect of polyoxometalates in catalysis is their inherent stability towards oxygen donors.[17–19] We used the Keggin-type diiron-substituted silicotungstate **1** (Figure 1) as a catalyst precursor for the selective epoxidation of alkenes with molecular oxygen at 1 atm and found that this epoxidation can be catalyzed with high TONs. The catalyst is thus able to use molecular oxygen as an oxidant, and raises the prospect of using this type of inorganic catalyst for industrial epoxidation processes.

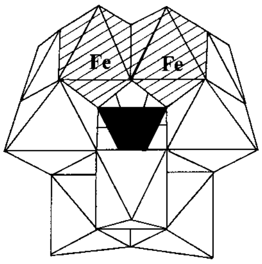

Figure 1. Polyhedral representation of γ-$SiW_{10}\{Fe^{3+}(OH_2)\}_2O_{38}^{6-}$ (**1**). The two iron atoms are represented by shaded octahedra. The WO_6 moieties occupy the white octahedra, and an SiO_4 group is shown as the internal black tetrahedron.

Figure 2 shows the time course of the oxygenation of cyclooctene with 1 atm of molecular oxygen catalyzed by **1** at 356 K. The average carbon balance for six runs was (100 ± 8) %. Cyclooctene oxide was selectively produced together with small amounts of 2-cycloocten-1-ol and 2-cycloocten-1-one. After 385 h, the conversion and selectivity for cyclooctene oxide reached 82 and 98 %, respectively, and the TON was 10000. The value is more than 100 times higher than those so far reported for the epoxidation of cyclooctene with 1 atm of molecular oxygen alone.[20]

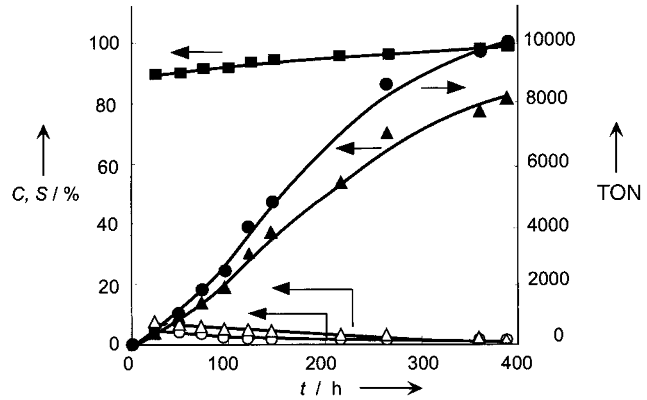

Figure 2. Oxygenation of cyclooctene with molecular oxygen catalyzed by **1** at 356 K. ▲, conversion of cyclooctene; ●, TON; ■, selectivity for cyclooctene oxide; ○, selectivity for 2-cycloocten-1-ol; △, selectivity for 2-cycloocten-1-one. Catalyst, 1.5 μmol; solvent, 1,2-dichloroethane/acetonitrile 1.5/0.1 mL; substrate, 18.5 mmol; p_{O_2} = 1 atm. C = conversion, S = selectivity.

Oxygenation of various alkenes with 1 atm of molecular oxygen was carried out in the presence of **1** at 356 K. Similarly to the oxygenation of cyclooctene, longer reaction periods increased the TON for each alkene. The results are summarized in Table 1. The main products were the corresponding

Table 1. Oxygenation of various alkenes with molecular oxygen catalyzed by **1** at 356 K.[a]

Substrate	TON	C [%]	Products	S [%]
cyclododecene	9600	74	cyclododecene oxide	64[b]
			2-cyclododecen-1-ol	31
			2-cyclododecen-1-one	5
cyclooctene	10000	82	cyclooctene oxide	98
			2-cycloocten-1-ol	1
			2-cycloocten-1-one	1
1-octene	2200	17	1,2-octene oxide	93
			1-octen-3-ol	5
			1-octen-3-one	2
2-octene (*cis*/*trans* = 8/2)	2500	20	2,3-octene oxide	94
			2-octen-4-ol	5
			2-octen-4-one	1
2-heptene (*cis*/*trans* = 8/2)	2900	24	2,3-heptene oxide	91
			2-hepten-4-ol	8
			2-hepten-4-one	1
2-hexene (*cis*/*trans* = 4/6)	1300	11	2,3-hexene oxide	79
			2-hexen-4-ol	19
			2-hexen-4-one	2

[a] Reaction conditions: catalyst, 1.5 μmol; solvent, 1,2-dichloroethane/acetonitrile, 1.5/0.1 mL; substrate, 18.5 mmol; p_{O_2} = 1 atm; reaction time, 385 h. The substrate/O_2 ratio in the gas phase may lie within the explosion limit. [b] Includes the selectivity for 1,2-cyclododecanediol (6 %).

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epoxides in all oxygenation reactions. This fact and the obtained TONs show that **1** can efficiently catalyze the epoxidation of various kinds of alkenes.

Keggin-type polyoxometalates show characteristic UV/Vis bands, and therefore their structures have often been characterized by UV/Vis spectroscopy. The UV/Vis spectrum of as-prepared **1** showed bands at 275 ($\varepsilon = 22600$), 334 (10000), and 470 nm (68 $\text{M}^{-1}\text{cm}^{-1}$), and after being used for the oxygenation of cyclooctene **1** showed the original absorption bands with almost the same intensities. The IR bands of the original skeletal vibration of **1** changed only slightly (see below). Magnetic susceptibility measurements and recording of Mössbauer and ^{183}W NMR spectra on the reaction solution to investigate the structure of **1** were thwarted by insufficient sensitivity at the low concentration (0.38 mM). After **1** (0.15 M) was treated with 1 atm of molecular oxygen in [D$_3$]acetonitrile for 96 h at 356 K, the ^{183}W NMR spectrum showed two broad signals at $\delta = -1330$ and -1840 with an integral ratio of 2:1, characteristic of the C_{2v} symmetry of the original γ-Keggin structure. This indicates that the two iron atoms occupy the same positions as shown in Figure 1 under the reaction conditions and that the structure of **1** is retained during the reaction. In addition, the fact that **1** is even stable in the presence of hydrogen peroxide,[21] as demonstrated by ^{183}W NMR spectrocopy, supports this conclusion.

The oxygenation of cyclooctene was not inhibited by the presence of 1–3 equiv (relative to **1**) of alkyl-radical scavengers such as *p-tert*-butylcatechol. For example, the conversion and selectivity for cyclooctene oxide after 96 h in the presence of 1 equiv of *p-tert*-butylcatechol were 20 and 92%, respectively. These values are in good agreement with those of 18 and 92%, respectively, in the absence of the radical scavenger. For epoxidation of *trans*- and *cis*-2-octenes, the *trans*/*cis*-oxide ratios were 10 and 0.2, respectively, that is, the reaction was rather stereospecific. Similarly, epoxidation of *cis*-2-hexene proceeded rather stereospecifically. In contrast, epoxidation via a radical intermediate proceeds nonstereospecifically. In fact, addition of a radical initiator, *N*-hydroxyphthalimide, mainly produced *trans*-2-octene oxide (*trans*/*cis* = 4) in the epoxidation of *cis*-2-octene. In addition, epoxidations of *cis*-2-octene and *cis*-2-hexene were faster than those of the corresponding *trans*-2-alkenes, as has been observed for epoxidation catalyzed by oxo iron porphyrins, which proceeds differently from epoxidation via a radical pathway.[22]

The kinetic studies showed zero-order dependence of reaction rates on the concentration of cyclooctene ([cyclooctene]), and first-order dependence on the concentration of **1** ([**1**]) and the partial pressure of molecular oxygen (p_{O_2}). These results indicate that the rate of decrease in [cyclooctene] is expressed by $-\text{d[cyclooctene]}/\text{d}t = k[\mathbf{1}]p_{\text{O}_2}[\text{cyclooctene}]^0$. Moreover, a maximum rate was obtained for $p_{\text{O}_2} = 1-2$ atm. The oxygenation of adamantane showed that the ratio of tertiary/secondary C–H bond selectivity on a per bond basis was 11.[23] Under free-radical conditions, the value is normally three, that is, different from that in the present system. All these results demonstrate that nonradical processes prevail to a major degree in the present system,[24] although some contribution of free radicals is still a possibility.

Figure 3 shows IR spectra of **1** after oxygenation of cyclooctene with ^{16}O$_2$ and ^{18}O$_2$ at 356 K. As-prepared **1** shows bands at 960 [ν(W=O$_{\text{terminal}}$)], 902, 884 [ν(SiO)], 800 (ν(W-O-W) for corner-sharing octahedra), and 753 cm^{-1} (ν(W-O-W) for edge-sharing octahedra). After **1** being used for the oxygenation of cyclooctene with ^{16}O$_2$, a new band was observed at 832 cm^{-1} (Figure 3a). It is reported that Fe=O bands appear in the range of 810–860 cm^{-1}.[22] After oxygenation with ^{18}O$_2$ a new band was observed at 776 cm^{-1} (Figure 3b). The shift of 56 cm^{-1} is in fair agreement with the expected shift of 48 cm^{-1}. The band disappeared after the reaction with cyclooctene under Ar, and cyclooctene oxide (1.9 equiv) was formed; this shows that the iron–oxygen species is reactive. The amount of H$_2$^{18}O produced was 2×10^{-4} mol, close to that of 2-cycloocten-1-one, and much less than that of cyclooctene oxide. In addition, the amount of cyclooctene oxide produced was about two times larger than the amount of O$_2$ consumed.[25] The above results show that the epoxidation proceeds without co-formation of water, and an intermediate iron–oxygen species is formed.

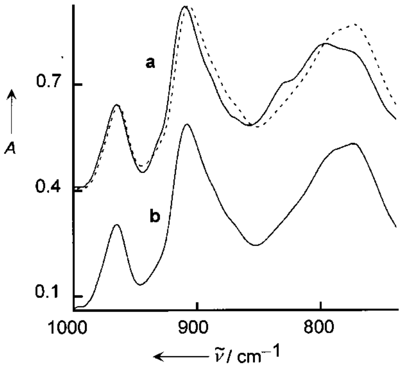

Figure 3. IR spectra of **1** after oxygenation of cyclooctene with ^{16}O$_2$ (a) and ^{18}O$_2$ (b and dotted line in a) for 96 h at 356 K. The spectra were measured by quickly evaporating the reaction solution, washing the resulting solid with diethyl ether, drying and then pressing it into a KBr pellet. A = absorbance.

In conclusion, we have demonstrated that **1** efficiently catalyzes the epoxidation of alkenes with molecular oxygen alone, a green route to epoxides. Detailed investigations on the reaction mechanism are in progress.

Experimental Section

The catalyst precursor **1** was synthesized as its tetrabutylammonium salt by the reported procedure:[26] A solution of K$_8$[γ-SiW$_{10}$O$_{36}$]·12H$_2$O (3.0 g, 1.0 mmol) in deionized water (30 mL) was quickly adjusted to pH 3.90 with concentrated nitric acid. Then, an aqueous solution of Fe(NO$_3$)$_3$·9H$_2$O (0.82 g, 2.0 mmol) in water (5 mL) was added. The color of the solution turned to pale yellow. After the solution had been stirred for 5 min, the addition of an excess of tetra-*n*-butylammonium nitrate (3.1 g, 10 mmol) resulted in a yellow-white precipitate. The precipitate was collected by filtration and purified by twice dissolving it in acetonitrile (15 mL) and adding water (300 mL) to reprecipitate the product. The yield of the purified compound was about 1.5 g (50%). The polyoxometalate γ-SiW$_{10}$\{Fe^{3+}(OH$_2$)\}$_2$O$_{38}$$^{6-}$ (**1**) has a γ-Keggin structure with C_{2v} symmetry, and the two iron centers occupy adjacent, edge-shared octahedra, as shown in Figure 1. UV/Vis, Mössbauer, EPR, and magnetic susceptibility data show that two high-spin Fe^{3+} centers are equivalent and antiferromagnetically coupled.[26]

Alkenes were distilled and treated with activated alumina to remove impurities and alkyl hydroperoxide. The reaction was carried out in a glass vial or a round-bottomed flask containing a magnetic stir bar under 1 atm of molecular oxygen as described previously.[21] 2-Cyclohexen-1-one was usually used as an internal standard. The homogeneous reaction solution was periodically sampled and analyzed by gas chromatography on a TC-WAX capillary column and by NMR spectroscopy. The amounts of oxygen consumed were measured with a gas burette. It was confirmed for the oxygenation of cyclooctene that no reaction proceeded without catalysts. Turnover numbers were calculated as moles of products per mole of **1**.

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[23] The oxygenation of adamantane was carried out under the following conditions: **1**, 11 μmol; solvent, 1,2-dichloroethane/benzene = 8 mL/2 mL; adamantane, 12.4 mmol; p_{O_2}, 1 atm; reaction temperature, 356 K; reaction time, 118 h. The conversion was 4% and the selectivities for 1-adamantanol, 2-adamantanol, and 2-adamantanone were 79, 11, and 10%, respectively.

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Cleavage of the C_{alkyl}–C_{aryl} Bond of [Pd–CH_2CMe_2Ph] Complexes**

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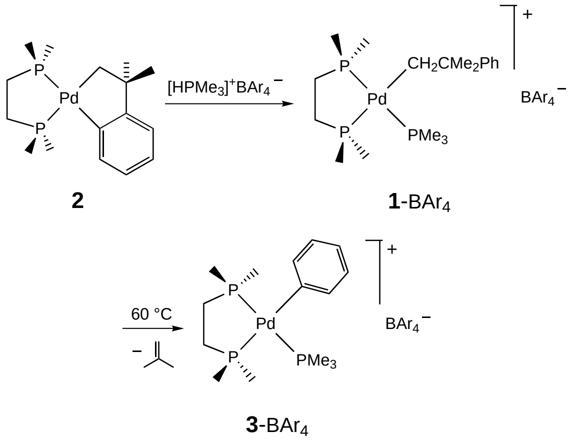
The cleavage and functionalization of strong C–C single bonds[1] by transition metal compounds is an important transformation,[2–6] which is relevant to Ziegler–Natta catalysis[7] and to other organometallic processes.[8, 9] Aryl elimination by activation of a β-C_{alkyl}–C_{aryl} bond[5] is the microscopic reverse of the migratory insertion of an alkene into a M–C_{aryl} bond, a relevant step of the Heck reaction[8] and of the SHOP process.[9] Herein we report on the conversion of a [Pd–CH_2CMe_2Ph]$^+$ moiety into the corresponding phenyl derivative, [Pd–Ph]$^+$, and the subsequent functionalization of the latter by conventional C_2H_4 migratory insertion chemistry to produce $C_6H_5CH{=}CH_2$.

The cationic complex [Pd(CH_2CMe_2Ph)(dmpe)(PMe_3)]$^+$ (**1**) (dmpe = $Me_2PCH_2CH_2PMe_2$) can be generated by reacting the palladacycle [Pd$\overline{CH_2CMe_2\text{-}o\text{-}C}{}_6H_4$)(dmpe)] (**2**)[10] with [$HPMe_3$]$^+$ BAr_4^- (Ar = 3,5-$C_6H_3(CF_3)_2$). At 60° C it under-



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Supporting information (kinetic data and reaction rates for the transformation **1** → **3** calyzed by **4**) for this article is available on the WWW under http://www.angewandte.com or from the author.