

Controlling Iron-Catalyzed Oxidation Reactions: From Non-Selective Radical to Selective Non-Radical Reactions

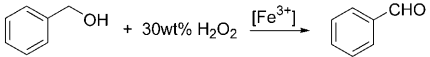
Feng Shi,^[a] Man Kin Tse,^[a, b] Zuopeng Li,^[c] and Matthias Beller*^[a, b]

Among all elements widely distributed in nature, iron is probably the most versatile and important redox center for life and natural transformation processes.^[1–2] With respect to sustainable chemistry and following nature's principles, iron is the ideal metal for more environmentally benign catalyst generations in future because of availability, low toxicity, and price. Although iron plays wonderfully in nature, the difficulty to prevent non-selective radical reactions makes its usage on laboratory scale, but especially for industrial production, more difficult—except being directly used as Lewis acid.^[3–5] In order to apply iron catalysts for a specific reaction with sufficient selectivity and activity, so far the general concept is based on the design of a suitable ligand which is further on optimized. In recent years iron catalysis has become a “hot topic” and notable progress has been accomplished applying this approach. For instance, novel iron containing systems have been developed for hydroxylation,^[6–8] sulfide oxidation,^[9–11] cross-coupling reactions,^[12–14] heterolytic RO–OH bond cleavage,^[15] hydroamination,^[16] allylic alkylation or amination,^[17–19] epoxidation,^[20–21] and alcohol oxidation.^[22–23] However, the intrinsic problem of non-selective radical side-reactions in the redox chemistry of iron has not been generally solved. This is especially evident for Fenton- or Gif-type reactions, that is, Fe^{n+} with H_2O_2 , which constitute one of the most famous iron salt-dependent

systems.^[24–28] Its high efficiency for oxidations of alkanes to ketones, benzene to phenol, and for environmental pollutant treatment has been extensively explored and has significant industrial potential.^[29–32] Notably, after more than a century of the first report, detailed investigations of the Fenton reaction still reveal two possible mechanisms,^[24–28] that is, the classical free radical mechanism and the oxygenated Fenton chemistry. Until today there is no concrete evidence to exclude each other completely, because both mechanisms have their own supporting evidence.^[24–28] In former reports, the importance of acids in Fenton chemistry has been studied,^[33–39] however a detailed study on the crucial function of pH variation on the catalyst activity and selectivity has been ignored.

Earlier on, we discovered the pH dependency of the selectivity in osmium-catalyzed dihydroxylations of olefins applying oxygen as the terminal oxidant.^[40] Based on our recent experience in iron catalysis,^[41–43] we supposed that the proton concentration in the reaction system might be also important for Fe-dependant oxidation reactions. Indeed, studying the oxidation of benzyl alcohol to benzaldehyde as a typical model reaction, a remarkable influence of the pH is observed (Table 1).

Table 1. Fe-catalyzed selective oxidation of benzyl alcohol.^[a]

			
Entry	KH_2PO_4 [mol %]	Conv. [%] ^[b]	Sel. (CHO/ CO_2H) [%] ^[c]
1	0	72	43 (81:19)
2	0.5	85	53 (77:23)
3	1.0	90	71 (75:25)
4	2.0	87	80 (75:25)
5	3.0	71	87 (70:30)
6	4.0	43	91 (56:44)
7	6.0	16	99 (50:49)

[a] Benzyl alcohol/ H_2O_2 / $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ / KH_2PO_4 1:1.5:0.02:0–0.06, solvent free; H_2O_2 was added with a syringe pump in 12 h. [b] Benzyl alcohol conversion. [c] Total selectivity to benzaldehyde and benzoic acid (ratio of benzaldehyde/benzoic acid).

[a] Dr. F. Shi, Dr. M. K. Tse, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de

[b] Dr. M. K. Tse, Prof. Dr. M. Beller
University of Rostock
Center for Life Science Automation (CELISCA)
Friedrich-Barnewitz-Str. 8, 18119 Rostock-Warnemünde (Germany)

[c] Z. Li
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences
Lanzhou, 730000 (China)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200801432>.

Initially, the correlation of acidity of the reaction system, catalyst activity and selectivity was investigated applying $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the catalyst and hydrogen peroxide as the oxidant in the presence of various concentration of KH_2PO_4 (Table 1). It is apparent that the selectivity of the reaction increased dramatically with increased concentration of KH_2PO_4 (Table 1, entries 1–7). Pure $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ gave a selectivity of only 43%. On the other hand, 99% selectivity is achieved when 6% KH_2PO_4 was added (Table 1, entries 1 and 7). Interestingly, also the activity of the catalyst increased adding a small amount of KH_2PO_4 . Hence, the conversion increased from 72 to 90% when 1% KH_2PO_4 was employed (Table 1, entries 1–3). However, when the KH_2PO_4 loading was further increased, the conversion decreased. Importantly, in the absence of KH_2PO_4 a significant amount of black tar polymer was obtained after removal of volatiles from the reaction mixture (Figure 1). It is of common knowledge that such tar polymers are produced by radical type reactions, for example, Fenton chemistry.^[30]

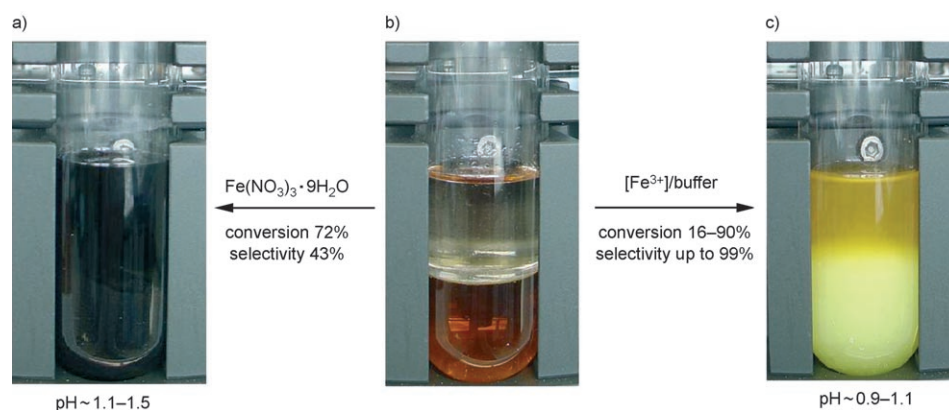


Figure 1. An illustration for the $[\text{Fe}^{3+}]$ and $[\text{Fe}^{3+}]/\text{buffer}$ catalyst system for selective oxidation of benzyl alcohol a) without pH control; b) before hydrogen peroxide addition, and c) precise pH control.

If the improved catalyst activity and selectivity originate from the different proton concentration and not because of the addition of KH_2PO_4 , other iron salts should also catalyze the reaction in similar manner. Hence, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FePO}_4 \cdot 4\text{H}_2\text{O}$, and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ were tested. KH_2PO_4 , H_2SO_4 and KHSO_4 were used to tune the pH of the system. Indeed, high selectivity to the aldehyde and acid was achieved and the catalyst activity is maintained (Table 2, entries 1–6).

In order to understand the effect of the additives, we measured the pH of the reaction systems.^[44] Surprisingly, the precise pH value of all the reactions with high conversion and selectivity is close to 1.00 (Table 1, entries 3 and 4, Table 2, entries 2, 4 and 6). At the same time, the deviation of the pH value (ΔpH) is close to 0.10. However, in reactions with lower selectivity ΔpH is significantly larger (>0.2).

Hence, we suppose that the catalyst activity is controlled by the absolute proton concentration (actual pH value),

Table 2. Iron-catalyzed oxidation of benzyl alcohol.^[a]

Entry	Iron salts	Additive [mol %]	Conv. [%] ^[b]	Sel. ($\text{CHO}/\text{CO}_2\text{H}$) [%] ^[c]
1	$\text{FePO}_4 \cdot 4\text{H}_2\text{O}$	0	8	99 (99:<1)
2	$\text{FePO}_4 \cdot 4\text{H}_2\text{O}$	2 H_2SO_4	80	90 (86:14)
3	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0	78	54 (83:17)
4	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	3 KH_2PO_4	74	84 (74:26)
5	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	0	84	69 (88:12)
6	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	0.7 KHSO_4	85	87 (81:19)

[a] Reaction conditions: See Table 1. [b] Benzyl alcohol conversion. [c] Selectivity to benzaldehyde and benzoic acid (ratio of benzaldehyde/benzoic acid).

while the selectivity is controlled by the change of pH value (ΔpH) during the reaction. If this hypothesis is right, the high selectivity should be independent of the pH value of the buffer and the nature of the buffer system. Thus, the activity of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the presence of various buffers was tested (Table 3). In fact all catalytic reactions gave high

selectivity (83–99%) if the ΔpH is ≤ 0.09 , albeit the absolute pH values. The conversion increased with an increasing acidity of the reaction system and reached ~90% (Table 4, entries 1–7). In the presence of SO_4^{2-} -based buffering systems, similar results are obtained (Table 4, entries 8 and 9). It is clearly shown that the pH and ΔpH but not the buffer composition is the key factors for the high activity and selectivity. It is important to note that all the buffered reaction systems kept homogeneous during the reaction; although FePO_4 precipitation is observed under solvent

free conditions (Table 1, entries 2–7, Table 2, entries 2 and 4). Under iron-free conditions at pH value lower than ~1.20

Table 3. Catalytic activity of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{buffer}$.^[a]

Entry	Buffer pH ^[b]	Conv. [%] ^[c]	Sel. ($\text{CHO}/\text{CO}_2\text{H}$) [%] ^[d]	ΔpH
1	0.38 (0.54/0.48)	87	86 (80:20)	0.06
2	0.61 (0.66/0.61)	87	85 (81:19)	0.05
3	0.78 (0.83/0.74)	86	83 (83:17)	0.09
4	1.00 (0.99/0.97)	85	87 (84:16)	0.02
5	1.19 (1.18/1.17)	82	85 (82:18)	0.01
6	1.39 (1.36/1.34)	38	84 (82:18)	0.02
7	2.00 (1.74/1.67)	27	89 (83:17)	0.07
8 ^[e]	1.00 (0.98/0.99)	87	88 (85:15)	0.01
9 ^[f]	0.98 (0.99/0.97)	89	89 (83:17)	0.02

[a] Reaction conditions: See Table 1. 5 mL buffer solution was used as the solvent. [b] pH value of buffer solution (pH value of buffer solution after the addition of reaction mixture before/after reaction).^[45] [c] Benzyl alcohol conversion. [d] Selectivity to benzaldehyde and benzoic acid (ratio of benzaldehyde/benzoic acid). [e] Buffer solution based on Na_2SO_4 . [f] Buffer solution based on K_2SO_4 .

also some conversion to unknown products is observed (5–20%). Here, no benzaldehyde or benzoic acid is formed (see Supporting Information, Table S1).

Table 4. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -catalyzed selective oxidation reactions.^[a]

Entry	Substrate	Buffer ([mL])	Conv. [%] ^[b]	Sel. [%] ^[c]
1	benzyl alcohol	–	73	40(83:17)
2		pH 0.99 (5)	77	85 (81:19)
3	benzene	–	25	<1
4		pH 0.99 (5)	<2	–

[a] Reaction conditions: See Table 1. [b] Benzyl alcohol or benzene conversion. [c] Selectivity to benzaldehyde and benzoic acid (ratio of benzaldehyde/benzoic acid) or phenol.

This indicates that side reactions are possibly caused by the acidic conditions but not from the iron catalyst itself. In agreement with our hypothesis, the selectivity of the reaction decreased at pH ~1.00 at lower concentration of the buffer. Variation of the concentration of buffer solutions from 0 to 0.4 M (based on PO_4^{3-}) showed that buffer strength of ~0.025 M of PO_4^{3-} was sufficient to provide high conversion with good selectivity (Table 5, entries 1–9).

Table 5. Effect of buffer concentration on the benzyl alcohol oxidation.^[a]

Entry	Buffer pH ^[b]	$c(\text{PO}_4^{3-})$ [mol L ⁻¹]	Conv. [%] ^[c]	Sel. (CHO/CO ₂ H) ^[d] [%]	ΔpH
1	6.69 (1.97/1.29)	0	97	48 (99:1)	0.68
2	1.01 (0.92/0.71)	0.003	96	55 (93:3)	0.21
3	1.02 (0.94/0.80)	0.006	97	70 (84:16)	0.14
4	1.02 (0.95/0.88)	0.013	97	72 (85:15)	0.07
5	0.98 (0.86/0.82)	0.025	94	82 (78:22)	0.04
6	0.98 (0.84/0.81)	0.050	92	87 (86:14)	0.03
7	1.02 (0.89/0.90)	0.100	87	89 (88:12)	0.01
8	1.02 (0.96/0.98)	0.200	87	89 (87:13)	0.02
9	0.99 (0.96/0.98)	0.400	83	88 (88:12)	0.02

[a] Reaction conditions: See Table 1. 5 mL buffer solution was used as the solvent. [b] pH value of buffer solution (pH value of buffer solution after the addition of reaction mixture before/after reaction).^[45] [c] Benzyl alcohol conversion. [d] Selectivity to benzaldehyde and benzoic acid (ratio of benzaldehyde/benzoic acid).

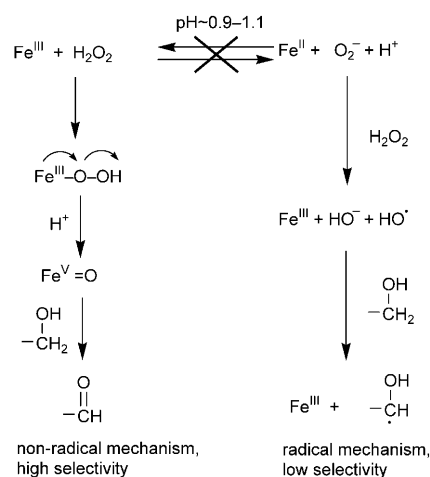
It is worth to note that the highest yield is achieved using a buffer composed with 0.05 M PO_4^{3-} . The pH value of the whole system, KH_2PO_4 , H_2SO_4 , and $\text{Fe}(\text{NO}_3)_3$, was ~0.8 and the ΔpH was only 0.03 (Table 5, entry 6). Again the result from the buffer free system suggests that a pH change during the reaction is favorable for radical generation reaction, that is, high activity but low selectivity (Table 5, entry 1).

Unexpectedly, omitting unwanted radical reactions by precise pH value control can be also applied in other typical radical systems, that is, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with hydrogen peroxide. Here, only 40% selectivity is obtained at 73% conversion (Table 4, entry 1). However, after the addition of 5 mL buffer (pH 0.99),^[45] the product yield is enhanced to 65 with 85% selectivity (Table 4, entry 2). From an industrial point

of view, it is important to note that also the inhibition of tar formation can be realized just through precise pH control.

Finally, we proved our theory in the benzene hydroxylation catalyzed by $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which is a classical radical initiated Fenton reaction. In the presence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as catalyst, benzene conversion was ~25% and less than 1% phenol is produced. A deep black reaction mixture formed and the side products are tar polymers. Parallel investigation of benzene oxidation under identical reaction conditions except for the presence of buffer showed complete inhibition of any radical type reaction (Table 4, entries 3 and 4).

Based on well defined Fenton and Gif reactions, the proposed mechanism of our reaction is shown in Scheme 1.^[24–28] As the production of tar polymers is significantly reduced in our system, the non-radical process is apparently the main pathway and the radical pathway is effectively inhibited by maintaining the pH value.



Scheme 1. Proposed mechanism for the Fe-catalyzed alcohol oxidation.

Direct evidence for this hypothesis was attained by cyclic voltammetry (CV) analysis of the reaction mixture (Figure 2). The reduction potential of Fe^{III} to Fe^{II} decreased from 0.14 to –0.23 V, which indicated that the reduction of Fe^{III} to Fe^{II} is minimized. Additionally, no oxidation peak of Fe^{II} to Fe^{III} is observed up to 1.2 V after the addition of KH_2PO_4 . Thus, the oxidation of Fe^{II} to Fe^{III} , which is responsible for the production of hydroxyl radicals, is inhibited. In other words, the catalytic cycle between Fe^{II} and Fe^{III} is blocked.

Kinetic studies of the oxidation of *para*-substituted benzyl alcohols showed that the rate determining step involves generation of a carbocation from the respective benzyl alcohol. The relative rate of oxidation of *para*-substituted benzyl alcohols to the corresponding benzaldehydes catalyzed by $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{KH}_2\text{PO}_4$ correlates with the Hammett σ_p with a large negative ρ (–2.5), which falls in the range of formal hydride equivalent abstraction by an electrophilic metal–oxo species and is significantly more negative than hydrogen atom abstraction (Figure 3).^[47–49]

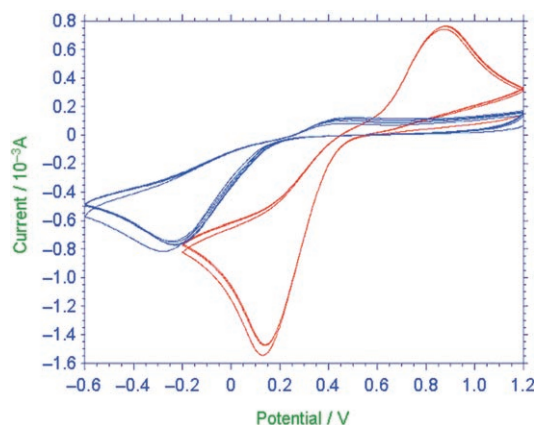


Figure 2. Cyclic voltammetry (CV) analysis of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + PhCH_2OH (red curve) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ + KH_2PO_4 + PhCH_2OH (blue curve). For the detailed information of the CV measurement, please see Supporting Information.

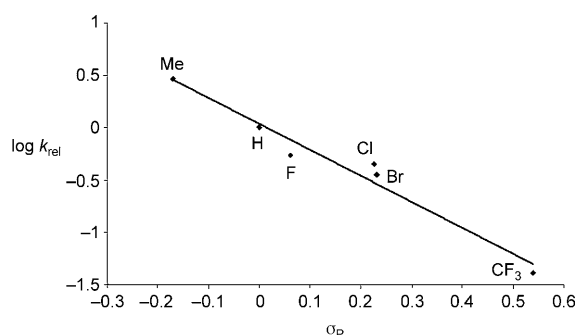
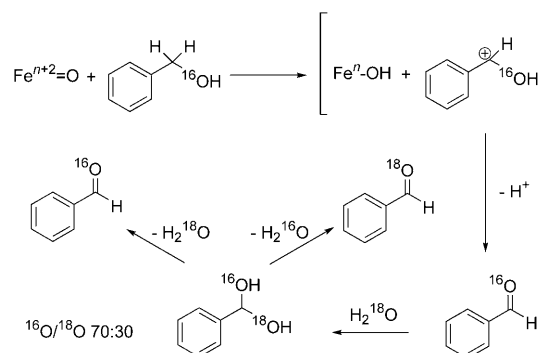


Figure 3. Hammett plot of $\log k_{\text{rel}}$ against substituent constants σ_p of benzyl alcohols.^[46]

In a competitive reaction of benzyl alcohol and $[\text{D}_7]$ benzyl alcohol, a kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) of 2.3 was observed, indicating the benzylic C–H bond breaking as the rate-determining step; this is consistent also with hydride equivalent abstraction but far smaller than hydrogen-atom abstraction by other metal–oxo complexes.^[47–53] Moreover, in the presence of >30 equivalent of H_2^{18}O to $\text{H}_2^{16}\text{O}_2$, the ratio of ^{16}O -benzaldehyde/ ^{18}O -benzaldehyde was 70:30 as determined by GC-MS measurements. In the control reaction, the ratio of ^{16}O -benzaldehyde/ ^{18}O -benzaldehyde was $46 (\pm 2.7):54 (\pm 2.7)$ and no ^{18}O -exchange of benzyl alcohol was observed. Hence, the isotope exchange mainly occurs after the formation of benzaldehyde. Therefore, the direct formation of PhCH^{16}O from the carbocation should be the main pathway. In agreement with studies of Fenton and Gif reactions,^[24–28] the kinetic studies here support the formation of high valent iron oxo species and the non-radical pathway is favorable (see Scheme 2).

In conclusion, for the first time the relationship between the absolute proton concentration (pH value), change of pH value (ΔpH) and catalytic performance in important iron-catalyzed selective oxidation reactions is demonstrated. It clearly shows that an increased proton concentration led to



Scheme 2. Proposed mechanism for the Fe-catalyzed alcohol oxidation to benzaldehyde.

higher catalyst activity and a small ΔpH during the reaction is responsible for improved selectivity. Essentially, iron oxo and radical pathways in iron-catalyzed redox reactions are switchable using ΔpH value as an on–off. Although we still cannot explain this phenomenon on a molecular level, we believe it is of general importance in oxidation chemistry and it should provide useful inspiration to rethink the mechanism of iron-catalyzed reactions, especially the century controversial mechanism of Fenton chemistry.

Experimental Section

General procedure for the selective oxidation of benzyl alcohol to benzaldehyde: All reactions were carried out applying a multi-reactor (Carousel 12 station, RADLEYS). Typically, 10 mmol benzyl alcohol (1.08 g), 0.2 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (80.8 mg), and 0–0.60 mmol KH_2PO_4 (0–81.6 mg) were added sequentially to a glass vessel ~50 mL. Then, the reaction mixture was vigorously stirred (500–750 rpm) at 75 °C. 15 mmol H_2O_2 (30wt% in water, from Merck, 1.5 mL) was added continuously with a syringe pump in 12 h. The mixture is cooled to room temperature and 1,4-dioxane (1760 mg, 20 mmol) is added for qualitative analysis by GC-FID. Depending on the pH the conversion was 16–90 % with a selectivity of 43–99 % (aldehyde and acid). For the detailed information of CV analysis, kinetic studies ($\log k_{\text{rel}}$ vs σ_p) and isotope effect studies see Supporting Information.

Acknowledgements

This work has been supported by the State of Mecklenburg-Western Pomerania, the Deutsche Forschungsgemeinschaft (SPP 1118 and Leibniz prize). Dr. Feng Shi thanks the Alexander-von-Humboldt-Stiftung for an AvH Fellowship.

Keywords: Fenton chemistry • heterogeneous catalysis • iron • pH control • radicals

- [1] E. V. Mielczarek, S. B. McGrayne, E. V. Mielczarek, S. B. McGrayne, *Iron, Nature's Universal Element: Why People Need Iron & Animals Make Magnets*, Rutgers University Press, New Brunswick, N.J., 2000.

- [2] R. M. Comell, U. Schwertmann, *The iron oxide: structures, properties, occurrences and uses*, Wiley-VCH, Weinheim, **2003**.
- [3] C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254.
- [4] M. Costas, K. Chen, L. Que, Jr., *Coord. Chem. Rev.* **2000**, *200*–202, 517–544.
- [5] M. Fontecave, S. MGNage, C. Duboc-Toia, *Coord. Chem. Rev.* **1998**, *178*–180, 1555–1572.
- [6] C. Kim, K. Chen, J. Kim, L. Que, Jr., *J. Am. Chem. Soc.* **1997**, *119*, 5964–5965.
- [7] M. Fujita, M. Costas, L. Que, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 9912–9913.
- [8] P. D. Oldenburg, A. A. Shteinman, L. Que, Jr., *J. Am. Chem. Soc.* **2005**, *127*, 15672–15673.
- [9] J. Legros, C. Bolm, *Chem. Eur. J.* **2005**, *11*, 1086–1092.
- [10] J. Legros, C. Bolm, *Angew. Chem.* **2004**, *116*, 4321–4324; *Angew. Chem. Int. Ed.* **2004**, *43*, 4225–4228.
- [11] J. Legros, C. Bolm, *Angew. Chem.* **2003**, *115*, 5645–5647; *Angew. Chem. Int. Ed.* **2003**, *42*, 5487–5489.
- [12] G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, *Angew. Chem.* **2007**, *119*, 4442–4444; *Angew. Chem. Int. Ed.* **2007**, *46*, 4364–4366.
- [13] M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 3686–3687.
- [14] A. Fürstner, A. Leitner, M. Méndez, H. Krause, *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863.
- [15] T. L. Foster, J. P. Caradonna, *J. Am. Chem. Soc.* **2003**, *125*, 3678–3679.
- [16] R. S. Srivastava, M. A. Khan, K. M. Nicholas, *J. Am. Chem. Soc.* **1996**, *118*, 3311–3312.
- [17] K. Komeyama, T. Morimoto, K. Takaki, *Angew. Chem.* **2006**, *118*, 3004–3007; *Angew. Chem. Int. Ed.* **2006**, *45*, 2938–2941.
- [18] B. Plietker, *Angew. Chem.* **2006**, *118*, 1497–1501; *Angew. Chem. Int. Ed.* **2006**, *45*, 1469–1473.
- [19] B. Plietker, *Angew. Chem.* **2006**, *118*, 6200–6203; *Angew. Chem. Int. Ed.* **2006**, *45*, 6053–6056.
- [20] N. A. Stephenson, A. T. Bell, *J. Am. Chem. Soc.* **2005**, *127*, 8635–8643.
- [21] G. Dubois, A. Murphy, T. D. P. Stack, *Org. Lett.* **2003**, *5*, 2469–2472.
- [22] M. Nakanishi, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 861–864.
- [23] S. E. Martín, A. Garrone, *Tetrahedron Lett.* **2003**, *44*, 549–552.
- [24] B. Halliwell, J. M. C. Gutteridge, *Free Radicals in Biology and Medicine*, 3rd, OUP, Oxford, **1999**.
- [25] D. H. R. Barton, D. K. Taylor, *Pure Appl. Chem.* **1996**, *68*, 497–504.
- [26] D. H. R. Barton, *Chem. Soc. Rev.* **1996**, *25*, 237–240.
- [27] P. A. MacFaul, D. D. M. Wayner, K. U. Ingold, *Acc. Chem. Res.* **1998**, *31*, 159–162.
- [28] D. T. Sawyer, A. Sobkowiak, T. Matsushita, *Acc. Chem. Res.* **1996**, *29*, 409–416.
- [29] T. Paczeński, A. Sobkowiak, *J. Mol. Catal. B J. Mol. Catal. A* **2003**, *194*, 1–11.
- [30] D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci, R. Vignola, *Angew. Chem.* **2000**, *112*, 4491–4493; *Angew. Chem. Int. Ed.* **2000**, *39*, 4321–4323.
- [31] S. Ito, A. Mitarai, K. Hikino, M. Hiram, K. Sasaki, *J. Org. Chem.* **1992**, *57*, 6937–6941.
- [32] C. K. Duesterberg, T. D. Waite, *Environ. Sci. Technol.* **2006**, *40*, 4189–4195.
- [33] T. Shiga, *J. Phys. Chem.* **1965**, *69*, 3805–3814.
- [34] S. J. Hug, O. Leupin, *Environ. Sci. Technol.* **2003**, *37*, 2734–2742.
- [35] J. A. Theruvathu, A. R. Flyunt, J. V. Sonntag, C. V. Sonntag, *J. Am. Chem. Soc.* **2001**, *123*, 9007–9014.
- [36] R. G. Zepp, *Environ. Sci. Technol.* **1992**, *26*, 313–319.
- [37] S. H. Bossmann, E. Oliveros, S. Göb, S. Siegwart, E. P. Dahlen, L. Payawan, Jr., M. Straub, M. Wörner, A. Braun, *J. Phys. Chem. A* **1998**, *102*, 5542–5550.
- [38] C. K. Duesterbergand, T. D. Waite, *Environ. Sci. Technol.* **2006**, *40*, 4189–4195.
- [39] S. Ito, A. Mitarai, K. Hikino, M. Hiram, K. Sasaki, *J. Org. Chem.* **1992**, *57*, 6937–6941.
- [40] a) C. Döbler, G. Mehlretter, M. Beller, *Angew. Chem.* **1999**, *111*, 3211–3212; *Angew. Chem. Int. Ed.* **1999**, *38*, 3026–3028; b) C. Döbler, G. Mehlretter, U. Sundermeier, M. Beller, *J. Am. Chem. Soc.* **2000**, *122*, 10289–10297; c) G. M. Mehlretter, C. Döbler, U. Sundermeier, M. Beller, *Tetrahedron Lett.* **2000**, *41*, 8083–8087.
- [41] a) G. Anilkumar, B. Bitterlich, F. G. Gelalcha, M. K. Tse, M. Beller, *Chem. Commun.* **2007**, 289–291; b) K. Schröder, X. Tong, B. Bitterlich, M. K. Tse, F. G. Gelalcha, A. Brückner, M. Beller, *Tetrahedron Lett.* **2007**, *48*, 6339–6342.
- [42] a) I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem.* **2005**, *117*, 3981–3985; *Angew. Chem. Int. Ed.* **2005**, *44*, 3913–3917; b) J. Kischel, D. Michalik, A. Zapf, M. Beller, *Chem. Asian J.* **2007**, *2*, 909–914; c) J. Kischel, K. Mertins, D. Michalik, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2007**, *349*, 871–875; d) S. Enthaler, G. Erre, M. K. Tse, K. Junge, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8095–8099; e) S. Enthaler, B. Hagemann, G. Erre, K. Junge, M. Beller, *Chem. Asian J.* **2006**, *1*, 598–604; f) J. Kischel, I. Iovel, K. Mertins, A. Zapf, M. Beller, *Org. Lett.* **2006**, *8*, 19–22; g) N. S. Shaikh, K. Junge, M. Beller, *Org. Lett.* **2007**, *9*, 5429–5432; h) S. Enthaler, B. Spilker, G. Erre, M. K. Tse, K. Junge, M. Beller, *Tetrahedron* **2008**, *64*, 3867–3876; i) N. S. Shaikh, S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 2531–2535; *Angew. Chem. Int. Ed.* **2008**, *47*, 2497–2501.
- [43] a) F. G. Gelalcha, B. Bitterlich, G. Anilkumar, M.-K. Tse, M. Beller, *Angew. Chem.* **2007**, *119*, 7431–7435; *Angew. Chem. Int. Ed.* **2007**, *46*, 7293–7296; b) F. Shi, M. K. Tse, M.-M. Pohl, A. Brückner, S. Zhang, M. Beller, *Angew. Chem.* **2007**, *119*, 9022–9024; *Angew. Chem. Int. Ed.* **2007**, *46*, 8866–8868.
- [44] Due to the nature of the solvent free and continuous hydrogen peroxide addition system, it is not convenient to measure the pH value in situ. Therefore, the pH value was determined in a series of model systems at room temperature.
- [45] The buffer solution composed by K_2HPO_4 and H_2SO_4 : the concentration of K_2HPO_4 was 0.40 mol L^{-1} . The pH value was then adjusted to lower pH value with 98wt% H_2SO_4 . The buffer solution composed by Na_2SO_4 or K_2SO_4 and H_2SO_4 : the concentration of Na_2SO_4 or K_2SO_4 was 0.60 mol L^{-1} . The pH value was then adjusted to lower pH value with 98 wt % H_2SO_4 .
- [46] The k_{rel} values were calculated by dividing k_{obs} of *para*-X-benzyl alcohol by k_{obs} of benzyl alcohol. See Supporting Information.
- [47] K. K. Banerji, *J. Chem. Soc. Perkin Trans. 2* **1973**, 435–437.
- [48] C.-M. Che, W.-T. Tang, W.-O. Lee, K.-Y. Wong, T.-C. Lau, *Dalton Trans.* **1992**, 1551–1556.
- [49] N. Y. Oh, Y. Suh, M. J. Park, M. S. Seo, J. Kim, W. Nam, *Angew. Chem.* **2005**, *117*, 4307–4311; *Angew. Chem. Int. Ed.* **2005**, *44*, 4235–4239.
- [50] R. C. Pratt, T. D. P. Stack, *J. Am. Chem. Soc.* **2003**, *125*, 8716–8717.
- [51] P. Chaudhuri, M. Hess, J. Müller, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **1999**, *121*, 9599–9610.
- [52] Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537–540.
- [53] L. Roecker, T. J. Meyer, *J. Am. Chem. Soc.* **1987**, *109*, 746–754.

Received: July 16, 2008

Published online: September 2, 2008

Please note: Minor changes have been made to this publication in *Chemistry—A European Journal* Early View. The Editor.