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Temperature effect on the epoxidation of olefins by an iron(III) porphyrin complex and *tert*-alkyl hydroperoxides

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An electron-deficient iron porphyrin complex catalyzes the epoxidation of olefins by *tert*-alkyl hydroperoxides *via radical-free* oxidation reactions in aprotic solvent; the epoxidation reactions were markedly influenced by reaction temperature and high yields of epoxide products were obtained with retention of stereospecificity at low temperature.

The reactions of iron(III) complexes of porphyrin and non-porphyrin ligands with alkyl hydroperoxides have been extensively studied as biomimetic models for heme- and non-heme-containing enzymes.[1] It has been shown in a number of reports that oxidation of hydrocarbons by iron(III) porphyrin complexes and *tert*-alkyl hydroperoxides proceeds *via* O–O bond homolysis (*i.e. free* alkoxyl radical chemistry) in aprotic solvents.[1–3] In addition, Ingold and coworkers evidenced, using 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) as a mechanistic probe to distinguish between *free* alkoxyl radical chemistry and *radical-free* chemistry, that O–O bond homolysis is a predominant pathway in non-porphyrin iron complex-catalyzed oxidation of hydrocarbons by *tert*-alkyl hydroperoxides.[1,4] Despite intensive study for the last two decades, it has rarely been observed that simple iron complexes of porphyrin and non-porphyrin ligands are able to catalyze the oxidation of hydrocarbons by alkyl hydroperoxides *via radical-free* chemistry in aprotic solvents.[5,6]† Since we found recently that a highly electron-deficient iron(III) porphyrin complex, $Fe(TF_4TMAP)(CF_3SO_3)_5$ [TF_4TMAP = *meso*-tetrakis(2,3,5,6-tetrafluoro-*N*,*N*,*N*-trimethyl-4-aniliniumyl)porphinato dianion], catalyzes the epoxidation and hydroxylation of hydrocarbons by H_2O_2 *via* radical-free oxidation reactions,[7] we attempted the epoxidation of olefins with the iron porphyrin complex and *tert*-alkyl hydroperoxides such as *tert*-butyl hydroperoxide (Bu^tOOH) and MPPH. Here we report that the epoxidation reactions were markedly influenced by reaction temperature and high yields of epoxide products with retention of stereospecificity were obtained at low temperature.

The catalytic epoxidation of cyclohexene by Bu^tOOH was carried out in the presence of $Fe(TF_4TMAP)^{5+}$ at various reaction temperatures under argon atmosphere in MeCN. As detailed in Table 1, the formation of cyclohexene oxide, cyclohexenol and *tert*-butyl cyclohexenyl peroxide (*c*-$C_6H_{11}OOBu^t$) was observed at room temperature, indicating that the cyclohexene oxidation proceeds *via* free alkoxyl radical chemistry (*i.e.* O–O bond homolysis of Bu^tOOH).[1,8] Interestingly, we found that the product distribution varied depending on reaction temperature. As the reaction temperature was lowered, the yields of cyclohexene oxide increased, while those of allylic oxidation products (*i.e.* cyclohexenol and *c*-$C_6H_{11}OOBu^t$) diminished (Table 1). These results indicate that the reaction of iron(III) porphyrin complex with Bu^tOOH is sensitive to reaction temperature and that two-electron epoxidation becomes a major pathway in the cyclohexene epoxidation at low temperature [Scheme 1(A), pathway A]. Further evidence that the epoxidation of olefins by $Fe(TF_4TMAP)^{5+}$ and Bu^tOOH at low temperature occurs *via* radical-free chemistry was obtained by analyzing products obtained in *cis*-stilbene epoxidation. *cis*-Stilbene was predominantly oxidized to *cis*-stilbene oxide [eqn. (1)],‡ demonstrating that the $Bu^tOO\cdot$ radical was not involved as an epoxidizing agent in the epoxidation reactions.[2,8]

The temperature effect on the reaction of $Fe(TF_4TMAP)^{5+}$ with alkyl hydroperoxides in MeCN was also observed when MPPH was used as an oxidant (Table 1). Only a small amount

Table 1 Epoxidation of cyclohexene by $Fe(TF_4TMAP)^{5+}$ and *tert*-alkyl hydroperoxides at various reaction temperatures in MeCN and in MeOH–CH_2Cl_2[a,b]

		Yields (%) of products formed in Bu^tOOH reactions[c,d]				Yields (%) of products formed in MPPH reactions[c]				
	T/°C	*t*/h	Cyclohexene oxide	Cyclohexenol	*c*-$C_6H_{11}OOBu^t$	*t*/h	Cyclohexene oxide	MPPOH	$PhCH_2OH$	PhCHO
MeCN	20	2	20 ± 3	29 ± 3	12 ± 5	2	7 ± 1	20 ± 3	63 ± 6	8 ± 4
	10	2	31 ± 3	22 ± 3	8 ± 4	2	12 ± 2	23 ± 3	47 ± 5	8 ± 3
	0	4	45 ± 4	18 ± 3	5 ± 3	4	17 ± 3	29 ± 3	33 ± 4	8 ± 2
	−10	4	52 ± 4	14 ± 2	< 2	4	32 ± 3	44 ± 4	27 ± 3	6 ± 2
	−20	4	70 ± 4	9 ± 2	< 2	5	38 ± 3	46 ± 5	18 ± 3	12 ± 4
	−30	4	74 ± 4	7 ± 2	0	6	46 ± 4	55 ± 6	12 ± 3	12 ± 4
MeOH–CH_2Cl_2[e]	20	2	59 ± 3	8 ± 2	Trace[f]	2	36 ± 2	47 ± 3	30 ± 3	Trace[f]
	10	2	70 ± 5	5 ± 1	Trace[f]	2	42 ± 3	45 ± 3	20 ± 2	Trace[f]
	0	4	68 ± 5	4 ± 2	Trace[f]	4	57 ± 4	62 ± 4	13 ± 2	Trace[f]
	−10	4	76 ± 5	< 2	Trace[f]	4	63 ± 5	69 ± 5	< 4	Trace[f]
	−20	4	75 ± 5	< 2	Trace[f]	5	68 ± 5	79 ± 6	< 4	Trace[f]

[a] MPPH[4] and *tert*-butyl cyclohexenyl peroxide (*c*-$C_6H_{11}OOBu^t$)[11] were prepared according to literature procedures. All reactions were run at least in triplicate, and the data represent the average of these reactions. [b] In a typical reaction, oxidant (2×10^{-2} mmol diluted in 80 μL of MeCN) was added to a reaction solution containing $Fe(TF_4TMAP)(CF_3SO_3)_5$ (1×10^{-3} mmol) and cyclohexene (0.3 mmol) in 0.3 mL MeCN at the given temperature under an inert atmosphere. After the reaction mixture was stirred for the given time, the reaction solution was directly analyzed by GC or GC–MS with known authentic sample. [c] Yields were based on oxidants added. [d] < 5% of cyclohexenone was formed in all of the reactions. [e] Since methanolysis of cyclohexene oxide took place under the reaction conditions, the yields of cyclohexene oxide were determined by summing the amounts of cyclohexene oxide and 2-methoxycyclohexanol.[12] [f] < 2% based on oxidant added was formed.

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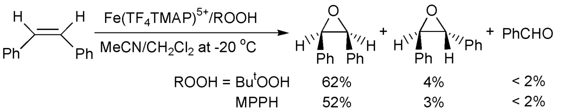
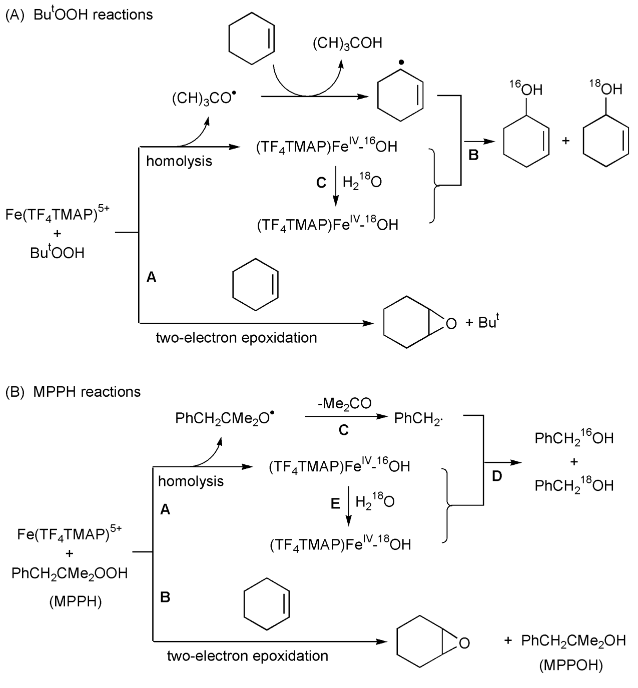


(1)

of cyclohexene oxide was formed and $PhCH_2OH$ was the major product derived from MPPH decomposition at room temperature. This result demonstrates that the reaction of $Fe(TF_4TMAP)^{5+}$ with MPPH occurs *via* O–O bond homolysis [Scheme 1(B), pathway A].[4] As the reaction temperature was lowered, the formation of cyclohexene oxide and $PhCH_2CMe_2OH$ (MPPOH) products increased, indicating that two-electron epoxidation takes place in the reaction of $Fe(TF_4TMAP)^{5+}$ and MPPH at low temperature [Scheme 1(B), pathway B]. When the epoxidation of *cis*-stilbene by $Fe(TF_4TMAP)^{5+}$ and MPPH was performed at low temperature, *cis*-stilbene oxide was obtained as a major product [eqn. (1)].‡ Also, MPPOH was the predominant product of MPPH decomposition (70% based on MPPH used). These results demonstrate unambiguously that the epoxidation of olefins by MPPH at low temperature occurs *via* radical-free chemistry.

Since it is known that methanol is a better solvent for iron porphyrin complex-catalyzed epoxidation of olefins by hydroperoxides,[5] the epoxidation of cyclohexene by Bu^tOOH and MPPH was carried out in a solvent mixture of MeOH and CH_2Cl_2 (3 : 1). As shown in Table 1, the yields of cyclohexene oxide formed in MeOH–CH_2Cl_2 were higher than those obtained in MeCN. In addition, as observed in the MeCN reactions, the oxide yields in the MPPH reactions increased as the reaction temperature was lowered. Interestingly, *ca.* 80% of MPPH was converted to MPPOH below −20 °C, and, to the best of our knowledge, this is the highest MPPOH formation in iron complex-mediated O–O bond cleavage of MPPH.[4]

We then studied ^{18}O-labeled water experiments in the epoxidation of cyclohexene by Bu^tOOH and MPPH,[9] in order to understand the source of oxygen atoms in cyclohexenol and benzyl alcohol products formed in the reactions of Bu^tOOH and MPPH, respectively.[4b,10] When the epoxidation reactions were carried out in the presence of $H_2{}^{18}O$ at room temperature,§ the percentages of ^{18}O incorporated from the labeled water into cyclohexenol and benzyl alcohol were 21 ± 2 and 14 ± 2%, respectively. The observation that some of the oxygen in the alcohol products came from $H_2{}^{18}O$ demonstrates unambiguously that cyclohexenyl and benzyl radicals were trapped by the $(TF_4TMAP)Fe^{IV}$–OH intermediate [pathway B in Scheme 1(A) and pathway D in Scheme 1(B)].[4b,9,10] The different and relatively small amounts of ^{18}O-incorporation into the cyclohexenol and benzyl alcohol products are ascribed to the fact that the oxygen exchange between the iron(IV)–OH intermediate and labeled water [pathway C in Scheme 1(A) and pathway E in Scheme 1(B)] is competing with the C–O bond-forming step between the intermediate and alkyl radicals [pathway B in Scheme 1(A) and pathway D in Scheme 1(B)].[3,9b]



Scheme 1

In conclusion, we have shown here that high yields of oxide products were formed *via* a *radical-free* mechanism in the epoxidation of olefins by *tert*-alkyl hydroperoxides at low temperature. The oxide yields were found to depend significantly on reaction temperature. In addition, it has been demonstrated unambiguously that alcohol products such as cyclohexenol and benzyl alcohol were formed by the trapping of alkyl radicals by $(TF_4TMAP)Fe^{IV}$–OH species. Future studies will focus on attempts to understand the temperature effect on the mechanism of hydroperoxide O–O bond activation by iron porphyrin complexes and to use the alkyl hydroperoxides in biomimetic alkane hydroxylation reactions.

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Notes and references

† Traylor *et al.* reported that epoxidation of olefins by electron-deficient iron(III) porphyrin complexes and Bu^tOOH gives high yields of oxide products in protic solvents (*i.e.* MeOH).[5] We have shown that the reactions of water-soluble iron(III) porphyrins with *tert*-alkyl hydroperoxides epoxidize olefins to give the corresponding oxide products in aqueous solution.[6]

‡ *Reaction conditions*: oxidant (2×10^{-2} mmol, diluted in 80 μL of MeCN) was added to a reaction solution containing $Fe(TF_4TMAP)^{5+}$ (3×10^{-3} mmol) and *cis*-stilbene (0.3 mmol) in a solvent mixture (1 mL) of MeCN and CH_2Cl_2 (1 : 1) at −20 °C. After stirring for 4 h, the reaction solution was directly analyzed by HPLC.

§ ^{18}O-labeled water experiments with Bu^tOOH and MPPH were performed at 20 °C under the same reaction conditions as described in footnote a of Table 1 except that $H_2{}^{18}O$ (25 μL, 95% ^{18}O enriched) was present in the reaction media. The ^{16}O and ^{18}O compositions in cyclohexenol and benzyl alcohol were determined by the relative abundances of mass peaks at *m/z* 83 and 85 for cyclohexenol and at *m/z* 108 and 110 for benzyl alcohol.

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