Reactivity of active oxygen species generated in the $EuCl_3$ catalytic system for monooxygenation of hydrocarbons

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The reactivity of active oxygen species generated from O_2 in the $EuCl_3$–Zn–$MeCO_2H$ catalytic system for the monooxygenation of various hydrocarbons has been studied in detail. In the case of the oxygenation of alkanes, a large difference between the reactivities of primary, secondary and tertiary C–H bonds (1 : 6 : 19) is observed. The kinetic isotope effect (KIE) between C–H and C–D (2.6) for the oxidation of cyclohexane, the relative conversion rate of cooxidation of cyclopentane and cyclohexane ($C_5/C_6 = 0.7$) and the non-retention of the configuration of tertiary C–H bonds suggest that the cleavage of the C–H bond is a key step in forming the alkyl radical intermediate by H˙ abstraction in the oxidation of alkanes. In the case of epoxidation of *cis*-hex-2-ene and *trans*-hex-2-ene, the *cis*- and *trans*-configurations are not preserved in their epoxides. This suggests that the epoxidation proceeds through alkyl radical intermediates. In the case of the hydroxylation of toluene, the regioselectivity in the formations of cresols (*o*:*m*:*p*, 13 : 1 : 16) suggests a strong electrophilicity of active oxygen species. The electrochemical studies for oxidation of cyclohexane mediated by $EuCl_3$ over a glassy carbon cathode suggest that the formation of Eu^{2+} and O_2^- is important for the cyclohexane oxidation.

Introduction

We have recently reported that europium salts (*e.g.* $EuCl_3$) are active catalysts for the monooxygenation of hydrocarbons with O_2 in the presence of Zn powder, carboxylic acid and solvent at room temperature.[1] Dioxygen, activated reductively with electrons and protons, was postulated to be responsible for the monooxygenation using this $EuCl_3$ catalytic system [eqn. (1)].

$$C_mH_n + O_2 + 2e^-(Zn) + 2H^+(MeCO_2H) \longrightarrow \cdots \longrightarrow C_mH_nO + H_2O + [Zn(MeCO_2)_2] \quad (1)$$

Other than $EuCl_3$, $LaCl_3$ and $SmCl_3$[2] also exhibited good activities for monooxygenations, although their catalytic activities were 10 times lower than that of $EuCl_3$.

We have reported the effects of reaction conditions [temperature, $P(O_2)$, solvent, carboxylic acid, *etc.*] on the oxygenation of cyclohexane and the epoxidation of hex-1-ene using these rare earth chloride based catalytic systems.[1] However, the following questions have not yet been answered; (*i*) why is there a large difference in reactivities between the $EuCl_3$ and $LaCl_3$ (or $SmCl_3$) catalytic systems?; (*ii*) are the catalytic natures and formulae of the active oxygen species different in each system?; and (*iii*) what properties are specific to this $EuCl_3$ catalytic system compared with the well-known oxygenation systems, such as the metalloporphyrin system,[3–10] the Fenton system[10,11] and the Gif system?[12–14] Therefore, the aim of this paper is to gain information about the nature of the active oxygen species and the reaction mechanism for the monooxygenation of alkanes and alkenes in the $EuCl_3$ catalytic system.

Results and discussion

Oxidation of alkanes

In order to gain information on the nature of active oxygen species in the rare earth catalytic system, the reactivities for the monooxygenation of some hydrocarbons were investigated for the $EuCl_3$, $LaCl_3$ and $SmCl_3$ catalytic systems. The active oxygen species in each catalytic system will be expressed as O*-$EuCl_3$, O*-$LaCl_3$ and O*-$SmCl_3$ hereafter.

As shown in Table 1, the oxygenation of hexane gave hexan-1-ol, hexanal, hexan-2-ol, hexan-2-one, hexan-3-ol and hexan-3-one for all catalytic systems. The turnover number (TON) of the sum of the products based on $EuCl_3$ was 6.57 in 1 h corresponding to 2.6% yield based on hexane. The regioselectivity of the active oxygen attacking the terminal and the internal C–H bonds of hexane was evaluated from the yield of oxygenated products. The ratio of the reactivities of primary to secondary (1° : 2°) C–H bonds (normalized per C–H bond) for O*-$EuCl_3$ was 1 : 6.0. For O*-$LaCl_3$ and O*-$SmCl_3$, the regioselectivities (1° : 2°) were 1 : 14.9 ($LaCl_3$) and 1 : 12.9 ($SmCl_3$), which differ appreciably from that observed in the $EuCl_3$ catalytic system.

The regioselectivity for the secondary : tertiary ratio (2° : 3°) was obtained from the oxygenation of adamatane. Although the concentration of adamantane used was 21 times lower than that of hexane, the TON for the sum of the products (adamantan-1-ol, adamantan-2-ol and adamantan-2-one) in the $EuCl_3$ catalytic system was 8.09 in 1 h corresponding to a yield of 66%. The ratio of the reactivity of the secondary and tertiary C–H bonds for the $EuCl_3$ catalytic system was 1 : 3.1. This ratio indicates that the nature of the reactivity of O*-$EuCl_3$ is quite different from that of Gif chemistry (2° : 3° 1 : ~1).[12–14] In the case of O*-$LaCl_3$ and O*-$SmCl_3$, the regioselectivities of secondary : tertiary were 1 : 6.3 ($LaCl_3$) and 1 : 6.8 ($SmCl_3$), though each TON for the sum of products was not over unity. The regioselectivities, primary : secondary : tertiary, estimated from the above results were for the $EuCl_3$ system, 1 : 6 : 19, for the $LaCl_3$ system, 1 : 15 : 94, and for the $SmCl_3$ system, 1 : 13 : 88. These ratios reflect the electrophilicities of the active oxygen species in each system.

The ratio of the initial conversion rates of cooxidation for cyclopentane and cyclohexane per C–H bond (C_5/C_6) obtained from their cooxidation gives further information about the active oxygen species.[15] It is reported that $C_5/C_6 \le 0.5$ suggests electrophilic attack on the C–H bond, $0.6 \le C_5/C_6 \le 1$ and $C_5/C_6 \ge 1$ indicate H˙ abstraction and H^- abstraction, respectively.[8,9,15] The results for the parameter of C_5/C_6 for $EuCl_3$, $LaCl_3$ and $SmCl_3$ catalytic systems obtained at a low conversion of reactants (*ca.* 0.1%) are shown in Table 1. The C_5/C_6 for $EuCl_3$ (0.66) was higher than that for $LaCl_3$ (0.38) and $SmCl_3$ (0.41). This result implies that H˙ abstraction occurs during the

Table 1 Oxygenation of alkanes catalysed by $EuCl_3$, $LaCl_3$ and $SmCl_3$[a]

Hexane	TON for product in 1 h						Yield/%	Remarks 1°:2°
	Hexan-1-ol	Hexan-2-ol	Hexan-3-ol	Hexanal	Hexan-2-one	Hexan-3-one		
$EuCl_3$	0.24	1.55	1.65	0.49	1.51	1.13	2.57	1:6.0
$LaCl_3$	0.01	0.11	0.12	0.02	0.22	0.15	0.25	1:14.9
$SmCl_3$	0.01	0.12	0.12	0.03	0.27	0.18	0.29	1:12.9

Adamantane[b]	TON for product in 1 h			Yield/%	2°:3°
	Adamantan-1-ol	Adamantan-2-ol	Adamantan-2-one		
$EuCl_3$	3.99	2.92	1.18	66.3	1:3.1
$LaCl_3$	0.55	0.18	0.08	6.64	1:6.3
$SmCl_3$	0.52	0.11	0.12	6.07	1:6.8

c-Pentane + c-Hexane[b]	TON for products				C_5/C_6
	c-Pentanone	c-Pentanol	c-Hexanone	c-Hexanol	
$EuCl_3$	0.028	0.101	0.035	0.169	0.66
$LaCl_3$	0.032	0.038	0.076	0.116	0.38
$SmCl_3$	0.035	0.040	0.075	0.116	0.41

[a] Standard conditions: $T = 40$ °C; catalyst (0.03 mmol); Zn (1 g); $MeCO_2H$ (2 ml); reactant (1 ml); CH_2Cl_2 (2 ml); O_2 (1 atm). [b] Adamantane (0.05 g) in CH_2Cl_2 (1 ml). [c] c-Pentane (0.5 ml) + c-hexane (0.5 ml).

Table 2 Retention of the configuration of the tertiary C–H bond of alkane during the oxidation[a]

	TON for products in 1 h (*trans*:*cis*)				
	1,2-Dimethylcyclohexan-1-ol	1,2-Dimethylcyclohexane 3-oxygenates	1,2-Dimethylcyclohexane 4-oxygenates	2-Methoxymethylcytohexane	Yield/%
cis-1,2-Dimethylcyclohexane					
$EuCl_3$	5.66 (48:52)	2.31 (7:93)	3.18 (2:98)	0.59 (20:80)	5.05
$LaCl_3$	1.01 (48:52)	0.02	0.04	0.0	0.46
trans-1,2-Dimethylcyclohexane					
$EuCl_2$	1.80 (48:52)	1.85 (97:3)	2.27 (99:1)	0.39 (89:11)	2.77
	Decalin-9-ol	Decalin 1-oxygenates	Decalin 2-oxygenates		Yield/%
cis-Decalin					
$EuCl_3$	1.54 (80:20)	1.17 (4:96)	1.81 (2:98)		2.09
trans-Decalin					
$EuCl_3$	1.04 (83:17)	2.45 (97:3)	3.13 (98:2)		3.16

[a] Standard conditions $T = 40$ °C; reaction time, 1 h; catalyst (0.03 mmol); Zn (1 g); $MeCO_2H$ (2 ml); reactant (1 ml); CH_2Cl_2 (2 ml); O_2 (1 atm).

oxidation of alkanes in the $EuCl_3$ catalytic system, while electrophilic attack on the C–H bond is suggested for the oxidations with O*-$LaCl_3$ and O*-$SmCl_3$. The strong electrophilicities of these active oxygen species have already been suggested from the ratios primary:secondary:tertiary described above.

It is suggested from the results of the C_5/C_6 factor that an alkyl radical intermediate may exist during the oxidation of alkanes with O*-$EuCl_3$. If this is true, then the *cis*- and *trans*-configuration of the cycloalkanes should not be retained in the products. Table 2 shows the results of the oxidations of *cis*- and *trans*-1,2-dimethylcyclohexane with O*-$EuCl_3$ and O*-$LaCl_3$. Although several oxygenated products of 1,2-dimethylcyclohexane were obtained, the most important concern was the ratio of *cis*- to *trans*-1,2-dimethylcyclohexan-1-ols. This ratio was 1:1.1 for both the oxidations of *cis*- and *trans*-1,2-dimethylcyclohexanes. The *cis*- and *trans*-isomerization of the dimethylcyclohexanes was not observed during the oxidation. These results indicate that the configuration of the tertiary C–H bonds is not retained in the oxidation with O*-$EuCl_3$. This result supports the hypothesis that an alkyl radical intermediate is produced as a result of H$^\bullet$ abstraction from the 1,2-dimethylcyclohexanes.

In the case of the oxidation of 1,2-dimethylcyclohexane with O*-$LaCl_3$, the ratio of *cis*- to *trans*-1,2-dimethylcyclohexan-1-ols was also 1:1.1, indicating the configuration of tertiary C–H bonds was not retained in this case either. This result may rule out the reaction mechanism suggested from the value of the C_5/C_6 factor; electrophilic attack at the C–H bond followed by insertion of oxygen between the C–H bond retaining the *cis*- and *trans*-configuration of the substrates in the 1,2-dimethylcyclohexan-1-ol. Thus, we believe that H$^\bullet$ abstraction is also important during the oxidation with O*-$LaCl_3$.

The original *cis*- and *trans*-retention in the products were also examined for the oxidations of *cis*- and *trans*-decalin with O*-$EuCl_3$. As can be seen from Table 2, the *trans*-form of decalin-9-ol was the major product for the oxidation of *cis*-decalin. The product ratio of *trans*- to *cis*-decalin-9-ols (80:20) for the oxidation of *cis*-decalin was close to the ratio obtained in the oxidation of *trans*-decalin (83:17). The retention of configuration was estimated to be about 3% from these *trans*- and *cis*-decalin-9-ol selectivities. This result also indicates that the *cis*- and *trans*-configuration of the reactants is not retained in the products, supporting the fact that H$^\bullet$ abstraction occurs during the oxidation of decalin.

Table 3 Oxidation of sulfur compounds and aromatics[a]

	TON for product in 1 h					
Diphenyl sulfide[b]	Ph_2SO	Ph_2SO_2	Total			Yield/%
$EuCl_2$	6.80	4.22	11.03			55.2
Diphenyl sulfoxide[c]		Ph_2SO_2				Yield/%
$EuCl_3$		6.97				35.0
Benzene	PhOH					Yield/%
$EuCl_3$	1.93					0.52
Toluene	Ph-		Cresols			
	CHO	CH_2OH	*o*-	*m*-	*p*-	Yield/%
$EuCl_3$	0.33	0.61	1.47	0.11	0.87	1.08

[a] Standard conditions: $T = 40$ °C; reaction time, 1 h; $EuCl_3$ (0.03 mmol), O_2 (1 atm); Zn (1 g); $MeCO_2H$ (2 ml); reactant (1 ml); CH_2Cl_2 (2 ml). [b] Ph_2S (0.112 g) in CH_2Cl_2 (1 ml). [c] Ph_2SO (0.121 g) in CH_2Cl_2 (1 ml).

The H$^{\bullet}$ abstraction in the C–H bond activation of alkanes was supported by kinetic isotope effect (KIE) experiments on the conversion rate of cyclohexane using a mixture of c-C_6D_{12} and c-C_6H_{12} under the standard conditions. A KIE of 2.6 was observed in the $EuCl_3$ catalytic system. This value was smaller than those in the $LaCl_3$ (3.7) and $SmCl_3$ catalytic systems (3.6). The results of the KIE suggest that either the cleavage of the C–H bond or H$^{\bullet}$ abstraction from cyclohexane is the rate determining step in the oxidations by these rare earth catalytic systems. The KIE obtained for O*-$EuCl_3$, O*-$LaCl_3$ and O*-$SmCl_3$ are different from those of Fenton (1.2),[10,11] Gif (2.3)[12–14] and metalloporphyrin (~5) systems.[3–9]

Oxidation of sulfur compounds and aromatics

Table 3 shows the reactivities of the $EuCl_3$ catalytic system for the oxidation of sulfur compounds and the hydroxylation of aromatics. The $EuCl_3$ catalytic system showed a high catalytic activity in the oxidation of diphenyl sulfide to diphenyl sulfoxide and diphenyl sulfone; total yield of 55% in 1 h based on diphenyl sulfide. Oxidation of Ph_2SO to Ph_2SO_2 also proceeded with O*-$EuCl_3$. The rate of oxidation of diphenyl sulfoxide was 37% lower than that of diphenyl sulfide. This result reflects the electrophilicity of O*-$EuCl_3$. Oxidation of diphenyl sulfide does not proceed with the Fenton system (HO$^{\bullet}$)[16] and the Gif system ($Fe^V{=}O$).[12] This oxidation is usually used as a test reaction of biomimetic systems, such as metalloporphyrin.[7,17] However, the oxidation of Ph_2SO to Ph_2SO_2 does not proceed in metalloporphyrin systems. Thus, the nature of O*-$EuCl_3$ and O*-$LaCl_3$ is different from that in these catalytic systems.

It is well known that the active oxygen species in the Fenton system (HO$^{\bullet}$)[10,11] and the metalloporphyrin system ($P^{\bullet +}$–$Fe^{4+}{=}O$)[3] initiate the hydroxylation of aromatics, but that in the Gif system ($Fe^{5+}{=}O$)[12–14] does not. The hydroxylation of benzene to phenol occurred with a TON of 1.93 in 1 h for the $EuCl_3$ catalytic system. The hydroxylation of toluene was carried out to obtain information on the regioselectivity for C–H bonds of the aromatic ring. The TON of 2.45 in 1 h for the cresols was larger than that for the hydroxylation of benzene. The ratio of regioselectivity for the formations of *o*-, *m*- and *p*-cresols per C–H bond was 13 : 1 : 16. A strong preference for the *o*- and *p*-orientations was observed. This result supports the electrophilic nature of O*-$EuCl_3$ suggested in the oxygenation of alkanes (Table 1).

Epoxidation of alkenes

Table 4 shows the results of the retention of configuration of the C=C bond for the epoxidation of stilbene and hex-2-enes. In the case of the epoxidation of *cis*-stilbene with O*-$EuCl_3$, a mixture of *cis*- and *trans*-stilbene oxide, along with products resulting from C=C bond cleavage (benzaldehyde and benzyl alcohol), were obtained. The ratio of *cis*- to *trans*-stilbene oxide was 2 : 98 when *cis*-stilbene was used as a starting material. Isomerization of *cis*-stilbene to *trans*-stilbene was not observed during the oxidation. These results suggest that the configuration of *cis*-stilbene is not retained in the epoxide for the $EuCl_3$ catalytic system. When the epoxidation of *cis*-stilbene was carried out at lower temperatures, the ratio of *cis* to *trans* increased to 13 : 87 (20 °C) and to 21 : 79 (0 °C). A slight increase in the selectivity to the sum of epoxide was observed with decreasing temperature from 43% (40 °C) to 53% (0 °C). These results suggest that part of the configuration of *cis*-stilbene was retained by decreasing the temperature. The epoxidation of *trans*-stilbene could not be carried out because *trans*-stilbene did not dissolve in the reaction mixture.

As mentioned above, most of the configuration of *cis*-stilbene was not retained. Therefore, to gain more information on the retention of configuration during the epoxidation, the reaction of *cis*- and *trans*-hex-2-enes with O*-$EuCl_3$ was studied in detail, as shown in Table 4. When the epoxidation of *cis*-hex-2-ene was carried out, *trans*- and *cis*-2,3-epoxyhexane, hexan-2-one, hexan-3-one and hexanediols were produced. The TON of 28.8 (10.6% yield) in 1 h for the sum of *cis*- and *trans*-epoxides (selectivity of 90%) was higher than that of 11.7 observed in the hex-1-ene epoxidation.[1] More selective and faster epoxidation of *cis*-hex-2-ene occurred compared with that of hex-1-ene (selectivity of 81%). The ratio of *cis*- to *trans*-2,3-epoxyhexane was 17 : 83 under the standard conditions. The results for the epoxidation of *trans*-hex-2-ene showed a TON of 24.1 (9.0% yield) in 1 h for the sum of the epoxides (selectivity of 90%) and the ratio of *cis* : *trans* was 9 : 91. The isomerizations of the reactant between *cis*- and *trans*-hex-2-enes were not observed during the epoxidation. These results suggest that part of the configuration of hex-2-ene is retained in the $EuCl_3$ catalytic system under the standard conditions because of the difference between the ratios of the epoxidation of *cis*-hex-2-ene (17 : 83) and *trans*-hex-2-ene (9 : 91) that was observed. The retention of the configuration was estimated to be about 8%. However, the majority of the configuration of hex-2-ene is not retained during the epoxidation. Influences of solvents (*e.g.* 1,2-dichloroethane) and carboxylic acids (*e.g.* propionic acid) on the ratios of *cis* : *trans* were studied. However, the ratios were constant, independent of the solvents and the acids. When the reaction temperature was decreased to 10 °C, the ratios of *cis* : *trans* did not change. This result seems to conflict with the result observed in the epoxidation of *cis*-stilbene. However, a rotation of the C–C bond of the intermediate from hex-2-enes may be easier than that of stilbene.

Table 4 Epoxidation of alkenes catalysed by the $EuCl_3$ system[a]

	TON for product in 1 h					
cis-Stilbene	*cis*-Stilbene oxide	*trans*-Stilbene oxide	Benzaldehyde	Benzyl alcohol	Yield/%	*cis*:*trans*
40 °C	0.14	6.08	7.30	1.04	7.73	2:98
20 °C	0.34	2.30	2.24	0.80	3.02	13:87
0 °C	0.29	1.02	0.87	0.29	1.31	21:79
cis-Hex-2-ene	*cis*-2,3-Epoxyhexane	*trans*-2,3-Epoxyhexane	Hexan-2-one	Hexan-3-one	Hexanediols	Yield/%	*cis*:*trans*
40 °C	4.83	24.0	0.24	0.13	0.95	11.72	17:83
With $EtCO_2H$	2.83	14.19	—	—	—	6.64	17:83
With $(CH_2Cl)_2$	4.61	24.2	0.24	0.13	0.97	11.72	16:84
10 °C	0.96	4.70	0.08	0.07	0.26	2.56	17:83
trans-Hex-2-ene							
40 °C	2.14	21.96	—	—	0.63	9.96	9:91
10 °C	0.39	4.31	0.09	0.08	0.16	2.18	8:92

[a] Standard conditions: $T = 40$ °C; reaction time 1 h; $EuCl_3$ (0.03 mmol); reactant (1 ml); O_2 (1 atm); Zn powder (1 g); $MeCO_2H$ (2 ml); CH_2Cl_2 (2 ml).

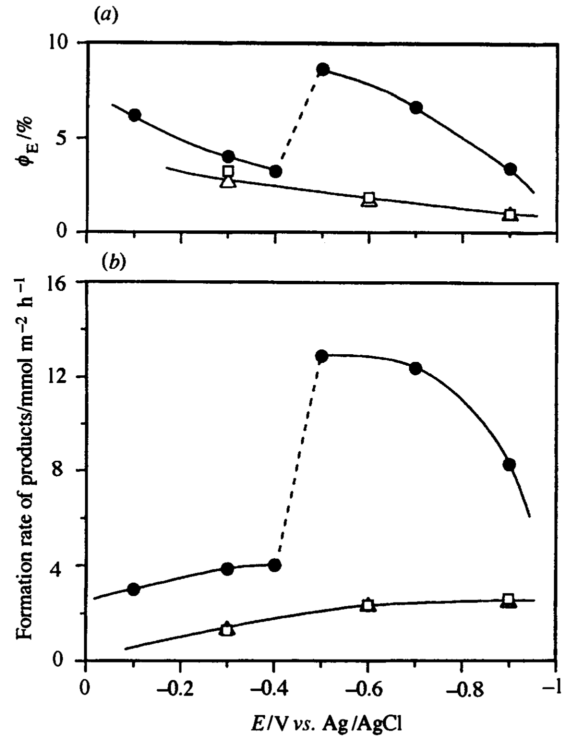


Fig. 1 Electrochemical oxidation of cyclohexane to cyclohexanone and cyclohexanol mediated by rare earth chlorides over a glassy carbon (GC) cathode; $T = 303$ K, GC cathode (5.0 cm^2), rare earth chlorides (2.0×10^{-3} mol l^{-1}), Bu'_4NClO_4 (0.2 mol l^{-1}, $MeCO_2H$ (7.0 mol l^{-1}), CH_2Cl_2 (6.2 mol l^{-1}), cyclohexane (1.85 mol l^{-1}), O_2 gas (5 ml min^{-1}); ● = $EuCl_3$, □ = $LaCl_3$, △ = $SmCl_3$

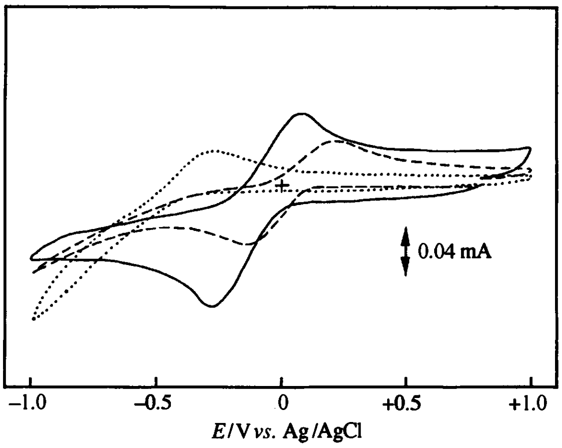


Fig. 2 Cyclic voltammetry of $EuCl_3$, $Eu(MeCO_2)_3$ and $Eu(ClO_4)_3$; scan rate 200 mV s^{-1}, $T = 303$ K, GC cathode (0.07 cm^2), rare earth chloride (2.0×10^{-3} mol l^{-1}), Bu'_4NClO_4 (0.2 mol l^{-1}), $MeCO_2H$ (7.0 mol l^{-1}), CH_2Cl_2 (8.05 mol l^{-1}), atmosphere of Ar; (*a*) (——) $EuCl_3$, (*b*) (- - - -) $Eu(MeCO_2)_3$ and (*c*) (– – –) $Eu(ClO_4)_3$

These results suggest that an alkyl radical intermediate is involved in the epoxidation. Generation of an alkyl radical intermediate may be responsible for the cleavage of the C=C bond of stilbene and styrene during the epoxidation and non-selective epoxidation of cyclohexene.[1]

Electrochemical study

In order to gain information on the oxidation state of europium, electrochemical studies have been carried out. Fig. 1 shows the oxygenation of cyclohexane as a function of the cathode potential. The oxidation of cyclohexane did not proceed at all in the absence of rare earth catalyst under the potential conditions in Fig. 1. The oxidation of cyclohexane to cyclohexanone and cyclohexanol occurred with addition of $EuCl_3$, $LaCl_3$ or $SmCl_3$. These results prove that $EuCl_3$, $LaCl_3$ and $SmCl_3$ work as mediators for the electrochemical oxygenation as shown in Fig. 1. In the case of $EuCl_3$, the rate of the oxygenation gradually increased with decreasing cathode potential from −0.1 to −0.4 V (*vs.* Ag/AgCl). When the potential decreased from −0.4 to −0.5 V, the rate of the oxygenation increased abruptly. In the case of $LaCl_3$ and $SmCl_3$, this sudden enhancement in the rate was not observed. The cathode potential for the sudden increase in the rate of oxygenation observed for $EuCl_3$ in Fig. 1 roughly corresponds to the standard redox potential of Eu^{3+}/Eu^{2+} (−0.55 V *vs.* Ag/AgCl). The standard redox potential of Sm^{3+}/Sm^{2+} (−1.75 V) is far more negative compared to that of Eu^{3+}/Eu^{2+}, and for La^{2+} does not exist. The results in Fig. 1 strongly suggest that the dramatic enhancement in the rate of oxygenation is due to electrochemical reduction of Eu^{3+} to Eu^{2+}.

To study further the electrochemical redox reactions of europium, we have measured cyclic voltammetry (CV) under similar conditions to those of potentiostatic studies. Fig. 2 shows the electrochemical redox reaction of some Eu salts [$EuCl_3 \cdot 6H_2O$, $Eu(MeCO_2) \cdot 6H_2O$ and $Eu(ClO_4)_3 \cdot 6H_2O$], in an atmosphere of Ar without addition of cyclohexane. A couple was not observed in the absence of Eu salts. Different CV spectra for the couples of Eu^{3+}/Eu^{2+} were observed for the three Eu salts. This suggests

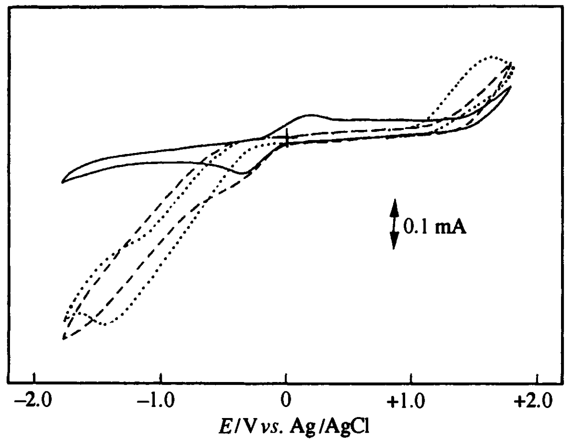


Fig. 3 Cyclic voltammetry of $EuCl_3$ and O_2; scan rate 200 mV s^{-1}, $T = 303$ K, GC cathode (0.07 cm^2), Bu'_4NClO_4 (0.2 mol l^{-1}), $MeCO_2H$ (7.0 mol l^{-1}), CH_2Cl_2 (6.2 mol l^{-1}), cyclohexane (1.85 mol l^{-1}); (*a*) (——) presence of $EuCl_3$ (2.0×10^{-3} mol l^{-1}) in an atmosphere of Ar, (*b*) (-----) without $EuCl_3$ in an atmosphere of O_2, (*c*) (– – –) presence of $EuCl_3$ (2.0×10^{-3} mol l^{-1}) in an atmosphere of O_2

that the counter-anion of Eu salts plays an important role in the active Eu species in the reaction mixture.

In the case of $EuCl_3$, a reduction peak of Eu^{3+} to Eu^{2+} at −0.28 V (*vs.* Ag/AgCl) and an oxidation peak of Eu^{2+} to Eu^{3+} at +0.05 V were observed. The difference between these peak potentials for the redox of Eu^{3+}/Eu^{2+}, $\Delta E_p = 0.33$ V, was 5.8 fold larger than the value estimated from theory for an electrochemically reversible system (0.0565 V). Thus, the redox reaction of Eu^{3+}/Eu^{2+} in this system is electrochemically irreversible; the rate of electrochemical reaction of Eu^{3+}/Eu^{2+} over the GC electrode was slow.

Fig. 3 shows some CV spectra in the presence of cyclohexane. The CV spectrum of (*a*) was measured for the redox reaction of $EuCl_3$ in an atmosphere of Ar. The reduction peak of Eu^{3+} to Eu^{2+} shifted to negative potential. The CV spectrum of (*b*) was measured in an atmosphere of O_2 without $EuCl_3$. Electrochemical reduction of O_2 to O_2^- over GC was observed (peak at −1.4 V),[19] with O_2^- being produced below −0.3 V. An oxidation peak of O_2^- was not observed because of the fast successive protonation and the formation of H_2O_2 [eqn. (2)].[19] The CV

$$O_2^- + H^+ \longrightarrow HO_2^{\bullet} \longrightarrow 1/2\, H_2O_2 + O_2 \qquad (2)$$

spectrum of (*c*) was measured in the presence of $EuCl_3$ in an atmosphere of O_2. The oxidation peak of Eu^{2+} to Eu^{3+} was not observed. This suggests that O_2^- is produced by the chemical reduction of O_2 with Eu^{2+} [eqn. (3)]. The reduction of O_2 was

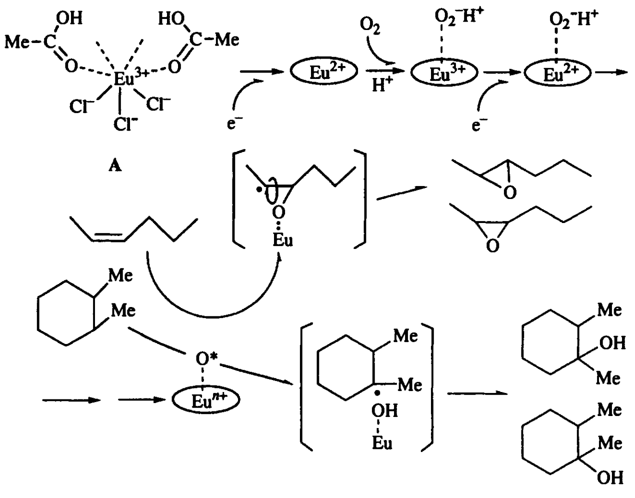
$$Eu^{2+} + O_2 \longrightarrow Eu^{3+} + O_2^- \qquad (3)$$

mediated by Eu^{3+}/Eu^{2+} reaction. In the cathode potential between −0.4 and −0.5 V, where the sudden increase in the oxidation activity was observed, the electrochemical formation of Eu^{2+} and O_2^- was observed.

The standard redox potential of Zn^{2+}/Zn^0 is −0.97 V (Ag/AgCl). Therefore, Eu^{3+} can be reduced to Eu^{2+} by Zn powder which is indispensable in the $EuCl_3$ system for the monooxygenations. The redox potential of Sm^{3+}/Sm^{2+} (−1.75 V) is far more negative than that of Zn^{2+}/Zn^0, and for La^{2+} does not exist. Thus, La^{2+} and Sm^{2+} cannot exist in their catalytic systems. Therefore, La^{3+} and Sm^{3+} should perform as catalysts in these catalytic systems.

Reaction scheme

A model of the active form of the europium catalyst, complex **A**, is shown in Scheme 1 and is proposed on the basis that the CV spectrum of $Eu(MeCO_2)_3$ is very different from that of $EuCl_3$ and the catalytic activity of $Eu(MeCO_2)_3$ is lower than that of $EuCl_3$.[1] The monooxygenation may be initiated by the active oxygen species generated from complex **A**.



Scheme 1

Eu^{2+} has an electron shell structure of $[Xe]4f^7$. Gd^{3+} has the same structure of $[Xe]4f^7$ but the catalytic activity of $GdCl_3$ was lower than those of $LaCl_3$ and $SmCl_3$. Therefore, the electronic structure of $[Xe]4f^7$ is not important and the redox reaction of Eu^{3+}/Eu^{2+} may be a key factor for the monooxygenation.

It is hypothesized that an O_2 coordinated on the Eu^{2+} of **A** is reductively activated, generating the active oxygen species. The reactivities of O^*-$EuCl_3$, O^*-$LaCl_3$ and O^*-$SmCl_3$ together with those of well-known systems are summarized in Table 5. Evidently, different reactivities are shown between O^*-$EuCl_3$ and O^*-$LaCl_3$ or O^*-$SmCl_3$. The electrophilicities of active oxygen species estimated from the ratios of primary : secondary : tertiary are $OH^{\bullet}$ (Fenton)[10,11] < O^*-$EuCl_3$ < O^*-$LaCl_3$, O^*-$SmCl_3$ < $RO_2^{\bullet}$(autooxidation)[5,18] < $P^{\bullet +}$–Fe^{4+}=O.[3–9] The results of the KIE, the C_5/C_6 factor and the retention of the substrate configuration in the products suggest that the cleavage of the C–H bond is the rate determining step and an alkyl radical intermediate is formed during the oxidation of alkanes in the rare earth catalytic systems. However, alkyl radical coupling products, such as dicyclohexyl or diadamantyl, were not produced.[1] This fact suggests that the $H^{\bullet}$ abstraction process might not simply be a metal-catalysed autoxidation. In the case of the epoxidation, the formation of the alkyl radical intermediates is proposed because the configuration of the substrate was not preserved during the epoxidation. However, the electrophilicity of O^*-$EuCl_3$ is proposed for the epoxidation because hex-2-enes are more reactive than hex-1-enes. These experimental facts indicate that the nature of the active oxygen generated in the rare earth catalytic system has both radical character and electrophilicity and is different from those of Fenton,[10,11] Gif[12–14] and metalloporpyrin systems.[3–9] This double character of O^*-$EuCl_3$ made it possible to oxygenate sulfur compounds and aromatics. It is not certain whether this double character of O^*-$EuCl_3$ comes from the unique active oxygen or from two independent species.

If the reduction of O_2 is caused by the oxidation of Eu^{2+}, $Eu^{3+}\cdots O_2^-$ (H^+) may be produced according to eqn. (4). A free

$$O_2 + Eu^{2+} + (H^+) \longrightarrow Eu^{3+}\cdots O_2^-(H^+) \qquad (4)$$

O_2^- or $HO_2^{\bullet}$ is not the active oxygen species for the monooxygenation because the very low reactivity of a free O_2^- or $HO_2^{\bullet}$ was previously reported.[19] It is suggested that the formation of Eu^{2+} and O_2^- over a GC cathode is important for the oxidation. We speculate that O_2^- or $HO_2^{\bullet}$ might be further activated

Table 5 Comparison for the reactivities of some catalytic oxidation systems

	Alkene	c-C_6H_{12}		Retention of configuration/%	
	1°:2°:3°	KIE	C_5/C_6	Alkane ox.	Alkene epox.
$EuCl_3$	1:6:19	2.6	0.66	0[h] 3[i]	8
$LaCl_3$	1:15:94	3.7	0.38	0[h] 3[i]	8
$SmCl_3$	1:13:84	3.6	0.41	*j*	*j*
$OH^{\cdot}$[a]	1:4.7:10	1.1	1.14	*j*	*k*
$RO_2^{\cdot}$[b]	1:18:134	1.0			
Gif[c]	1:3:~3	2.0~2.3	0.6~0.85	*j*	*k*
Fe–TPPCl					
(PhIO)[d]	1:25:150	6~9	*j*	90	~100
(O_2, Zn, $MeCO_2H$)[e]		2.3	0.45	0	*j*
Mn–TPPCl					
(PhIO)[f]	1:59:600	2~5	*j*	*j*	~100
(O_2, Zn, $MeCO_2H$)[g]	(—):1:20	2.8	0.7	25%	>90

[a] From refs. 8, 9, 11 and 12. [b] Refs. 4 and 16. [c] Refs. 11 and 12. [d] Ref. 3. [e] Ref. 7. [f] Refs. 5 and 6. [g] Ref. 6. [h] Obtained from the *cis*- and *trans*-1,2-dimethylcyclohexane oxidation. [i] Obtained from the *cis*- and *trans*-decalin oxidation. [j] Not measured. [k] The reaction does not proceed.

through a redox reaction of Eu^{3+}/Eu^{2+} [eqn. (5)]. However, the

$$Eu^{3+}\cdots O_2^-(H^+) + e^- \longrightarrow Eu^{2+}\cdots O_2^-(H^+) \times (\longrightarrow\longrightarrow O^{*}\text{-}Eu^{3+}) \quad (5)$$

definitive form of the active oxygen cannot be identified at this moment.

Further investigations are needed to clarify the working state of the Eu species, the nature of the active oxygen species in $EuCl_3$, $LaCl_3$ and $SmCl_3$ systems and the reaction mechanisms for the monooxygenations.

Experimental

General procedure and materials

The standard procedure for the monooxygenation of hydrocarbons was as follows. Rare earth salts were dissolved in a stirred solution of carboxylic acid, as a proton donor, and a solvent in a three-necked flask with a reflux condenser. Then a reactant and Zn powder, as an electron donor, was added to the solution and the reaction was started by stirring the mixture with a magnetic stirrer under a stream of O_2 at 40 °C. The reaction was continued for 1 h. All the reagents were commercial products (Tokyo Kasei, Wako Pure Chemical and Aldrich), used without further purification. The products were analysed by gas chromatography (Shimazu GC-14A) with PEG-20M over OV-1 capillary columns (0.25 mm i.d. × 25 m).

Regioselectivity of the primary, secondary and tertiary C–H bonds

The regioselectivities were estimated from the product yields of the oxidations of hexane and adamantane per C–H bond. The oxidations were carried out as below; $EuCl_3\cdot 6H_2O$, $LaCl_3\cdot 6H_2O$ or $SmCl_3\cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (2 ml, 7.06 mol l^{-1}) and CH_2Cl_2 (2 ml) in a flask. Then, hexane (1 ml, 1.53 mol l^{-1}) or adamantane solution (0.05 g in CH_2Cl_2 of 1 ml, 7.40×10^{-2} mol l^{-1}) and Zn (1.0 g, 15.3 mmol) was added to the mixture. The reaction was allowed to continue under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h. The products were analysed by GC. The ratios of primary:secondary and secondary:tertiary were defined as shown in eqns. (6) and (7).

$$\text{Primary:secondary} = \frac{[\text{hexan-1-ol} + \text{hexan-1-al}]/6}{[\text{hexan-2-ol} + \text{hexan-2-one} + \text{hexa-3-nol} + \text{hexan-3-one}]/8} \quad (6)$$

$$\text{Secondary:tertiary} = \frac{[\text{adamantan-2-ol} + \text{adamantan-2-one}]/12}{[\text{adamantan-1-ol}]/4} \quad (7)$$

The C_5/C_6 parameter[15]

The parameter of C_5/C_6 was estimated from the initial conversion rates of the cooxidation for cyclopentane and cyclohexane per C–H bond. The cooxidation was carried out as below; $EuCl_3\cdot 6H_2O$, $LaCl_3\cdot 6H_2O$ or $SmCl_3\cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (2 ml, 7.06 mol l^{-1}) and CH_2Cl_2 (2 ml) in a flask. Then, a mixture of c-C_5H_{10} (0.5 ml, 1.06 mol l^{-1}) and c-C_6H_{12} (0.5 ml, 0.926 mol l^{-1}) and Zn (1.0 g, 15.3 mmol) were added to the mixture. The reaction continued under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h. The products were analysed by GC. The parameter of C_5/C_6 was defined as shown in eqn. (8), where

$$C_5/C_6 = \frac{([\text{c-}C_5H_9OH + \text{c-}C_5H_8O]/10)[C_5H_{10}]^0}{([\text{c-}C_6H_{11}OH + \text{c-}C_6H_{10}O]/12)/[C_6H_{12}]^0} \quad (8)$$

$[C_5H_{10}]^0$ and $[C_6H_{12}]^0$ are the initial concentrations of c-C_5H_{10} and c-C_6H_{12}, respectively.

Retention of configuration for the alkane oxidation

The retention of configuration for tertiary C–H bonds was studied during the oxidations of *cis*- and *trans*-dimethylcyclohexanes and *cis*- and *trans*-decalins. The oxidations were carried out as detailed below. $EuCl_3\cdot 6H_2O$ or $LaCl_3\cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (7.06 mol l^{-1}) and CH_2Cl_2 (2 ml). Then *cis*-dimethylcyclohexane (1 ml, 1.39 mol l^{-1}), *trans*-dimethylcyclohexane (1 ml, 1.43 mol l^{-1}), *cis*-decalin (1 ml, 1.30 mol l^{-1}) or *trans*-decalin (1 ml, 1.26 mol l^{-1}) and Zn (1.0 g, 15.3 mmol) were added to the mixture. The reaction continued under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h. The products were analysed by GC.

Measurement of kinetic isotope effects

The kinetic isotope effects (KIE) were measured for the oxidation of cyclohexane by GC–mass spectrometry (Shimadzu QP2000A). A detailed experimental procedure has already been reported.[1,2] The oxidations were carried out as detailed below. $EuCl_3\cdot 6H_2O$, $LaCl_3\cdot 6H_2O$ or $SmCl_3\cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (7.06 mol l^{-1}) and CH_2Cl_2 (2 ml). Then, a mixture of c-C_6D_{12} (0.5 ml, 0.924 mol l^{-1}) and c-C_6H_{12} (0.5 ml, 0.926 mol l^{-1}) and Zn (1.0 g, 15.3 mmol) were added to the mixture. The reaction continued under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h.

Oxidation of sulfur compounds

The oxidations of Ph_2S and Ph_2SO were carried out as detailed below. $EuCl_3 \cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (2 ml, 7.06 mol l^{-1}) and CH_2Cl_2 (2 ml). Then, Ph_2S solution (0.112 g in 1 ml CH_2Cl_2, 0.12 mol l^{-1}) or Ph_2SO solution (0.121 g in 1 ml CH_2Cl_2, 0.12 mol l^{-1}) and Zn (1.0 g, 15.3 mmol) were added to the mixture. The reaction was allowed to continue under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h. The products were analysed by GC.

Hydroxylation of benzene and toluene

The hydroxylations were carried out as detailed below. $EuCl_3 \cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (2 ml, 7.06 mol l^{-1}) and CH_2Cl_2 (2 ml). Then, benzene (1 ml, 2.22 mol l^{-1}) or toluene (1 ml, 1.88 mol l^{-1}) and Zn (1.0 g, 15.3 mmol) were added to the mixture. The reaction was allowed to continue under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h. The products were analysed by GC.

Retention of configuration for epoxidations

The retention of configuration for C=C bonds was studied during the epoxidation of *cis*-stilbene and *cis*- and *trans*-hex-2-enes. The oxidations were carried out as detailed below. $EuCl_3 \cdot 6H_2O$ or $LaCl_3 \cdot 6H_2O$ (0.03 mmol, 6.00×10^{-3} mol l^{-1}) was dissolved in a solution of $MeCO_2H$ (7.06 mol l^{-1}) and CH_2Cl_2 (2 ml). Then, *cis*-stilbene (1 ml, 1.13 mol l^{-1}), *cis*-hex-2-ene (1 ml, 1.63 mol l^{-1}) or *trans*-hex-2-ene (1 ml, 1.61 mol l^{-1}) and Zn (1.0 g, 15.3 mmol) were added to the mixture. The reaction was allowed to continue under a stream of O_2 (1 atm, 5 ml min^{-1}) at 40 °C for 1 h. The products were analysed by GC.

Electrochemical oxidation

A conventional electrochemical cell with the cathode and the anode separated by sintered glass was used for the electrochemical oxidation of cyclohexane. A glassy carbon (5 cm^2) cathode, a Pt-black/Pt-plate anode and a Ag/AgCl [0.197 V *vs.* normal hydrogen electrode (NHE)] reference electrode were used for these experiments. The composition of the catholyte (25 ml) was $EuCl_3$ (2.00×10^{-3} mol l^{-1}), $Bu^t_4NClO_4$ (0.20 mol l^{-1}), $MeCO_2H$ (7.06 mol l^{-1}), CH_2Cl_2 (6.20 mol l^{-1}) and cyclohexane (1.85 mol l^{-1}). O_2 gas (5 ml min^{-1}) was bubbled into the catholyte in the cathode. The cathode potential was controlled by a potentiostat (HOKUTO Co., HA-301) and a function generator (HB-104).

Measurement of cyclic voltammetry (CV)

CV spectra of $EuCl_3$, $Eu(ClO_4)_3$ and $Eu(MeCO_2)_3$ were measured using the same cell with a GC working-electrode (0.07 cm^2) under similar conditions to those described above. The scan rate was 200 mV s^{-1}.

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