

Catalysis of Sm^{3+} for the oxidation of alkanes with O_2 in the liquid phase

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Abstract

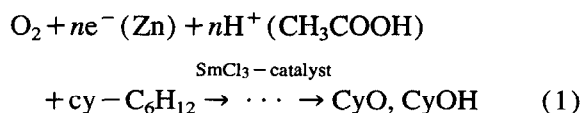
The catalysis of Sm^{3+} for oxidation of alkanes was studied in detail. The optimum reaction conditions were suggested for the oxidation of cyclohexane to cyclohexanone and cyclohexanol catalyzed by Sm^{3+} in the liquid phase (SmCl_3 , reactant, carboxylic acid, Zn, O_2 , solvent, and H_2O). Combination of acetic acid and dichloromethane was the most suitable for the oxidation. The active oxygen in SmCl_3 -catalytic system exhibited good catalytic activities for the oxidation of hexane and adamantane. However, low products yield was obtained for the hydroxylation of benzene. Large difference observed in the reactivities of primary, secondary and tertiary carbons of alkanes, $1^\circ:2^\circ:3^\circ = 1:13:88$, suggested that the active oxygen in SmCl_3 -catalytic system has a strong electrophilicity in its nature. Large isotope effect ($k_{\text{H}}/k_{\text{D}} = 3.6$) was observed for the oxidation of a mixture of $\text{cy-C}_6\text{D}_{12}$ and $\text{cy-C}_6\text{H}_{12}$ with the active oxygen in SmCl_3 -catalytic system.

Keywords: Adamantane; Alkanes; Cyclohexane; Hexane; Oxygenation; Samarium

1. Introduction

We have recently reported the homogeneous catalytic oxidation of cyclohexane to cyclohexanol (CyOH) and cyclohexanone (CyO) with O_2 in the presence of SmCl_3 [1], and the electrocatalytic oxidation of alkanes and aromatics over the graphite-supported SmCl_3 (SmCl_3/Gr) cathode during H_2 - O_2 fuel cell reactions [2]. It is unusual that Sm^{3+} , a rare earth element, catalyzes the oxidation of alkanes at ambient temperature. Components of our homogeneous reaction system are SmCl_3 , cyclohexane, O_2 , Zn, CH_3COOH , CH_2Cl_2 , and H_2O , which are similar to those in Gif(IV) system [3] except for using FeCl_3 (catalyst) and

pyridine (solvent). In our system, a reductively activated dioxygen with electrons (from Zn powder) and protons (from CH_3COOH) in SmCl_3 -catalytic system, was postulated to be responsible in the partial oxidation of cyclohexane to CyO and CyOH (Eq. 1). However, the details for the oxidation in SmCl_3 -catalytic system have not been described.



The first aim of this paper is to show the effects of each component on the oxidation of cyclohexane catalyzed by SmCl_3 to obtain a whole picture of the oxidation. The second is to examine whether the reactivity of the active oxygen in the SmCl_3 -

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catalytic system is comparable to that of the active oxygen on Sm/Gr cathode [2] and those of other active oxygen species in the well-known systems, such as free HO \cdot system [4], metal–porphyrin system (Por \cdot +Fe^{IV}=O) [5], and Gif(IV) system (Fe^V=O) [3].

2. Experimental

The standard experimental procedure for the oxidation of cyclohexane was as follows. SmCl₃·6H₂O (16.5 μ mol = 6 mg) was dissolved in a mixed-solution of CH₃COOH (2 ml), H₂O (0.1 ml) and CH₂Cl₂ (2 ml) in a three necked flask (100 ml) with a reflux condenser. After cyclohexane (1 ml) and Zn powder (1.0 g) had been added to the solution, the reaction was started by stirring the solution and the slurry with a magnetic stirrer under a stream of O₂ (1 atm, 5 ml STP·min⁻¹) at 40°C. The reaction was continued for 1 h.

Adamantane oxidation was carried out using the solutions of adamantane (0.05 g) and CH₂Cl₂ (1 ml) instead of cyclohexane (1 ml). For the oxidations of hexane and benzene, pure reactants of 1 ml was used instead of cyclohexane. Other reaction conditions were the same as the standard ones for the oxidation of cyclohexane.

For the quantitative analysis of the products, the crude reaction mixture after the reaction was treated as follows: (a) CH₂Cl₂ (10 ml) was added to the reaction vessel. (b) The reaction mixture and slurry were filtered and the residue was washed with CH₂Cl₂ (10 ml). (c) NaOH aq. (10 wt%, 10 ml) was added to the filtrate (20 ml) and shaken vigorously, separating the organic layer. (d) The products dissolved in the aqueous layer were extracted with CH₂Cl₂ (10 ml \times 3). (e) The product solutions (organic extracts from (c) and (d)), to each of which was added an internal standard (1-adamantanol, 1 μ mol), were analyzed by a gas chromatography (Shimazu GC-14A) and a GC–mass spectrometer (Shimazu QP2000A) with PEG-20M and OV-1 capillary columns (0.25 mm i.d. \times 25 m).

The oxidation of cyclohexane using a mixture of cy-C₆D₁₂ (0.5 ml) and cy-C₆H₁₂ (0.5 ml) was carried out for the experiment of kinetic isotope effect. The products were analyzed by GC–mass spectrometer. Kinetic isotope effect was estimated from the areas of peaks of m/z = 57, 61, 55 and 58. These peaks were identified as below; m/z (57) as the fragment (CH₂=CH-CH=OH⁺) of cy-C₆H₁₁OH, m/z (61) as the fragment (CD₂=CD-CD=OH⁺) of cy-C₆D₁₁OH, m/z (55) as the fragment (CH₂=CH-C \equiv O⁺) of cy-C₆H₁₀O, m/z (58) as the fragment (CD₂=CD-C \equiv O⁺) of C₆D₁₀O [2,6].

3. Results and discussions

3.1. Time course

Fig 1. shows kinetic curves for the oxidation of cyclohexane under standard reaction conditions. The products were cyclohexanone (CyO), cyclohexanol (CyOH) in the liquid phase, and CO₂ in the gas phase, other products such as dicyclohexyl and cyclohexanediol were not detected. The selectivity to CO₂ based on carbon was 16%. However, an equal amount of CO₂ was produced without addition of cyclohexane. This observation

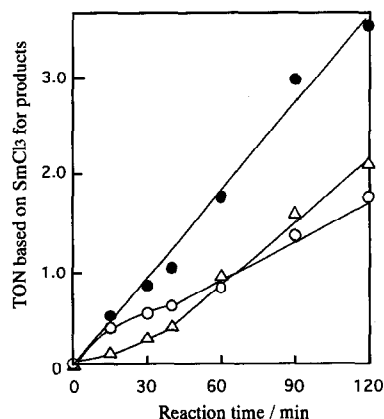
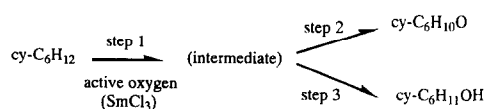


Fig. 1. Kinetic curves of the oxidation of cyclohexane catalyzed by Sm³⁺ in the liquid phase. Experimental conditions: $T = 40^\circ\text{C}$, SmCl₃·6H₂O 6 mg, cyclohexane 1 ml, CH₃COOH 2 ml, CH₂Cl₂ 2 ml, H₂O 0.1 ml, Zn powder 1 g, $P(\text{O}_2)$ 1 atm. (Δ) cyclohexanone, (\circ) cyclohexanol, (\bullet) total.



Scheme 1.

Table 1
Effect of solvents on the oxidation of cyclohexane

Run	Solvent	TON ^a		
		CyO	CyOH	Total
1	dichloromethane	0.97	0.89	1.86
2	1,2-dichloroethane	0.10	0.56	0.66
3	pyridine	~0	0.20	0.20
4	acetonitrile	~0	0.05	0.05
5	diethyl ether	0.08	0.01	0.09

^a TON; turnover number based on Sm^{3+} for the products for 1 h, CyO cyclohexanone, CyOH cyclohexanol. $T=40^\circ\text{C}$, time = 1 h. Each solvent 2 ml, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ 6 mg, cyclohexane 1 ml, CH_3COOH 2 ml, H_2O 0.1 ml, O_2 1 atm, Zn powder 1.0 g.

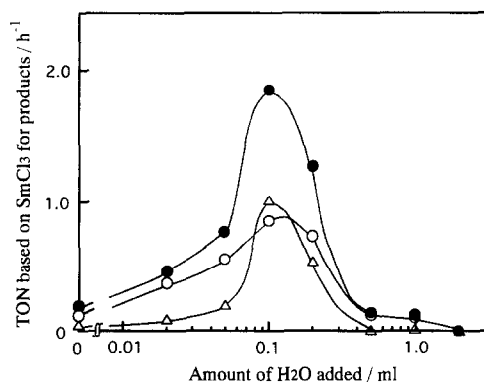


Fig. 2. Effect of the amount of H_2O added on the oxidation of cyclohexane catalyzed by Sm^{3+} in homogeneous system. Experimental conditions: $T=40^\circ\text{C}$, time = 1 h, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ 6 mg, cyclohexane 1 ml, CH_3COOH 2 ml, CH_2Cl_2 2 ml, Zn powder 1 g, $P(\text{O}_2)$ 1 atm. (Δ) cyclohexanone, (\circ) cyclohexanol, (\bullet) total.

suggests that CO_2 forms from CH_3COOH or CH_2Cl_2 . Thus, cyclohexane was oxidized selectively to CyO and CyOH. Turnover number based on Sm^{3+} (TON) for sum of the products linearly increased with reaction time. TON at 2 h was 3.5 that corresponded to the yield based on cyclohexane of 0.63%. No induction period was observed in the oxidation of cyclohexane (sum of CyOH and CyO). However, the selectivities to CyOH and CyO varied considerably because the forma-

tion of CyO showed an induction period at the reaction time < 1 h. The oxidation of cyclohexane produced steadily after 1 h holding roughly constant selectivities to CyO (54%) and CyOH (46%). When a mixture of CyOH (15 μmol) and cyclohexane (1 ml) as a starting material for the oxidation, CyO formation was not accelerated to compare with that of the standard conditions, and addition of CyO to the starting material also did not accelerate the CyOH formation. These observations suggest that CyO and CyOH are produced in parallel (Scheme 1).

3.2. Optimum reaction conditions

Solvent effect. Table 1 shows the catalytic activities for the oxidation of cyclohexane using several different solvents. Fairly good TON for sum of the products was obtained by using dichloromethane and 1,2-dichloroethane. However, these TON for sum of the products using pyridine (to be an effective solvent in Gif(IV) system [3]), acetonitrile, and diethyl ether were very low. These observations suggest that the solvents having low coordination affinity are suitable for the oxidation of cyclohexane in our system.

Fig. 2 shows the effect of H_2O on the oxidation using CH_2Cl_2 solvent. The amount of H_2O addition affected TON for sum of the products considerably. TON was very low when H_2O was not added. TON increased with increasing the amount of H_2O added. The maximum TON was obtained with H_2O addition of 0.1 ml. The selectivity to CyO increased with increasing the amount of H_2O addition at ≤ 0.1 ml. However, an excess addition of $\text{H}_2\text{O} > 0.1$ ml decreased the product yield. The agglomeration of Zn powder to a ball shape was observed during the oxidation when an excess H_2O was added ($\text{H}_2\text{O} > 0.1$ ml).

Effect of carboxylic acids. Table 2 shows the results of the oxidation of cyclohexane using different carboxylic acids (2 ml) instead of CH_3COOH . The oxidation of cyclohexane was observed using propanoic acid, butyric acid and iso-butyric acid. The maximum TON for sum of the products was obtained by using CH_3COOH

Table 2
Effect of carboxylic acids on the oxidation of cyclohexane ^a

Run	Carboxylic acids	TON		
		CyO	CyOH	Total
1	HCOOH	0	0	0
2	C ₂ H ₅ COOH	0.23	0.70	0.93
3	C ₃ H ₇ COOH	0.02	0.14	0.16
4	C ₂ H ₄ (CH ₃)COOH	~0	0.07	0.07
5	CH ₃ COOH	0.95	0.80	1.75
6	CH ₃ COOH (1 ml)	0.23	0.43	0.66
7	CH ₃ COOH (4 ml)	0.59	1.02	1.61
8	CH ₃ COOH (6 ml)	0.50	1.05	1.55

^a T = 40°C, time = 1 h. Each carboxylic acid 2 ml for runs 1 to 5, SmCl₃·6H₂O 6 mg, cyclohexane 1 ml, CH₂Cl₂ 2 ml, H₂O 0.1 ml, O₂ 1 atm, Zn powder 1.0 g.

(run 5). The order of TON for each carboxylic acids does not correspond to that of pK_a (25°C) for each acid, acetic acid (4.76) < butyric acid (4.82) < iso-butyric acid (4.85) < propanoic acid (4.87). The carboxylic groups of each acid can coordinate to Sm³⁺ which was speculated to be active species responsible for the oxidation of cyclohexane. When formic acid was used (run 1), little decomposition of formic acid was observed. This must explain the absence of the oxidation of cyclohexane. The results in run 5–8 show the effect of the amount of CH₃COOH added (1–6 ml) on the oxidation. The maximum TON was obtained at CH₃COOH addition of 2 ml and the selectivity to CyO showed the maximum at this amount.

Effect of reactant concentration. Dependence of the amount of cyclohexane added (0.1–2 ml) on TON were studied. TON for sum of the products increased with increasing the amount of cyclohexane addition. The maximum TON was obtained with cyclohexane addition of 1.5 ml. The product selectivities did not depend on the concentration of cyclohexane. TON decreased unusually with excess addition of cyclohexane of 2 ml. During this experiment, we observed that the reaction mixture separated into two layers. This might have reduced the TON unexpectedly.

Effect of amount of Zn powder. The oxidation of cyclohexane did not occur when Zn powder

was omitted. TON for sum of the products linearly increased with increasing amount of Zn powder at ≤ 1.0 g. The addition of excess Zn powder (> 1.0 g) exhibited only a small increase in the product yield, because some of the Zn powder was exposed to the gas phase which would not effectively work as a reducing agent. Most of the added Zn powder remained after the oxidation for all the experiments (0.5 g ≤ Zn ≤ 2.0 g). Thus, the increase in TON may be ascribed to the increase in the effective surface area of Zn powder, accelerating the generation of the active oxygen species.

Effect of O₂ pressure. Fig. 3 shows the effect of the partial pressure of O₂ on the oxidation of cyclohexane. The oxidation did not occur in the absence of O₂. TON for the sum of the products increased with increasing the pressure of O₂. The selectivity to CyO increased considerably with increasing pressure of O₂. CyO and CyOH may be produced in parallel, as described earlier (Scheme 1). The rate of generation of the active oxygen must be increased with increasing the pressure of O₂, accelerating the rate of oxidation of cyclohexane (step 1 in Scheme 1) which would be the rate-determining step for the formation of CyOH and CyO as described later. The selectivities of the products in Fig. 3 propose that the rate of step 2 in Scheme 1 is accelerated relatively

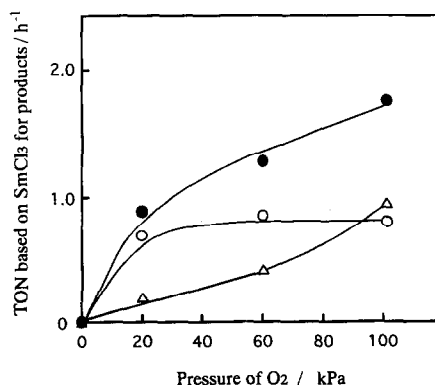


Fig. 3. The oxidation of cyclohexane catalyzed by Sm³⁺ as a function of the partial pressure of O₂ in a homogeneous system. Experimental conditions: T = 40°C, time = 1 h, SmCl₃·6H₂O 6 mg, cyclohexane 1 ml, CH₃COOH 2 ml, CH₂Cl₂ 2 ml, H₂O 0.1 ml, Zn powder 1 g. (△) cyclohexanone, (○) cyclohexanol, (●) total.

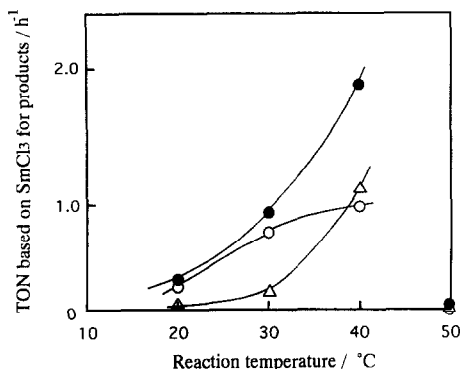


Fig. 4. Temperature dependence on the oxidation of cyclohexane catalyzed by Sm^{3+} in homogeneous system. Experimental conditions: Time = 1 h, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ 6 mg, cyclohexane 1 ml, CH_3COOH 2 ml, CH_2Cl_2 2 ml, H_2O 0.1 ml, Zn powder 1 g, $\text{P}(\text{O}_2)$ 1 atm. (Δ) cyclohexanone, (\circ) cyclohexanol, (\bullet) total.

faster than that of step 3 with increasing the pressure of O_2 .

Temperature dependence. TON for the products as functions of reaction temperature are shown in Fig. 4. TON for sum of the products increased with a rise in reaction temperature. The oxidation of cyclohexane did not occur at the temperatures above the boiling point of CH_2Cl_2 (40.5°C). Thus, 40°C was the optimum temperature for the oxidation of cyclohexane in Fig. 4. The steep increase in the selectivity to CyO with a rise in reaction temperature indicates that the activation energy for step 2 in Scheme 1 is larger than that for step 3.

3.3. Reactivity of the active oxygen in SmCl_3 -catalytic system

Table 3 shows the reactivities of different substrates with the active oxygen in SmCl_3 -catalytic system.

It is noted that the active oxygen in SmCl_3 -catalytic system exhibited the poor catalytic activity for the oxidation of benzene, producing a small amount of phenol but not hydroquinone. It has been reported that the hydroxylation of benzene occurred over SmCl_3/Gr cathode [2]. The catalytic activity of SmCl_3/Gr for the benzene hydroxylation was close to that for the cyclohexane oxidation. The reactivity of the active oxygen in

SmCl_3 -catalytic system for the hydroxylation of benzene in Table 3 was lower than that observed in SmCl_3/Gr cathode. It is well known that the active oxygen species in Fenton system (HO^\cdot) [4] and in metal-porphyrin system ($\text{Por} \cdot + \text{Fe}^{\text{IV}}=\text{O}$) [5] exhibit a good catalytic activity for the hydroxylation of benzene, but that in Gif-Orsay-Texas system ($\text{Fe}^{\text{V}}=\text{O}$) [3] was not effective.

The oxidation of adamantane occurred with the active oxygen in SmCl_3 -catalytic system, producing 1-adamantanol, 2-adamantanol, and 2-adamantanone. TON for sum of the products was 1.3 that corresponded to the yield based on adamantane of 6%. To get the information of the regioselectivity for the oxidation of adamantane, the regioselectivity was evaluated from the ratio of TON for the secondary products (2-adamantanol + 2-adamantanone) per C–H bond (12) and that of the tertiary product (1-adamantanol) per C–H bond (4), denoted as $2^\circ:3^\circ$. The ratio was evaluated as 1:6.8 for the active oxygen in SmCl_3 -catalytic system. The active oxygen does not have such a specific reactivity observed in Gif(IV) system ($2^\circ:3^\circ > 1:0.3$) [3].

The oxidation of hexane also occurred, producing 1-hexanol, hexanal, 2-hexanol, 2-hexanone, 3-hexanol, and 3-hexanone. TON for sum of the products was 1.3 (yield based on hexane of 0.3%). The active oxygen has a high potential for the oxidation of alkanes, since the reactivity of hexane is believed to be far less than that of cyclohexane. The regioselectivity was defined as the ratio of TON for primary product (1-hexanol + hexanal) per C–H bond (6) and that of secondary products (2-, and 3-hexanols + 2-, and 3-hexanones) per C–H bond (8), denoted as $1^\circ:2^\circ$, this ratio for the active oxygen in the SmCl_3 -catalytic system was 1:12.9.

The regioselectivity to 1° , 2° , 3° for SmCl_3 -catalytic system estimated from the results described above was 1:13:88. The order of electrophilicity for active oxygen species in each systems was free HO^\cdot system (1:4.7:10) < SmCl_3/Gr cathode system (1:4.8:13) < SmCl_3 -catalytic

Table 3
Reactivities of active oxygen in SmCl₃-catalytic system ^a

Reactant	TON	Remarks
benzene	phenol (0.39)	
adamantane ^b	2-adamantanol (0.19), 2-adamantanone (0.21), 1-adamantanol (0.93)	2°:3° = 1:6.8
hexane	1-hexanol (0.02), 2-hexanol (0.23), 3-hexanol (0.23), hexanal (0.05), 2-hexanone (0.49), 3-hexanone (0.32)	1°:2° = 1:12.9
cy-C ₆ H ₁₂ + cy-C ₆ D ₁₂ ^c	cy-C ₆ H ₁₁ OH (79.8 ^d), cy-C ₆ D ₁₁ OH (37.3 ^d), cy-C ₆ H ₁₀ O (100.0 ^d), cy-C ₆ D ₁₀ O (21.5 ^d)	k _H /k _D = 3.6

^a T = 40°C, time = 1 h, SmCl₃·6H₂O 6 mg, reactant 1 ml, CH₃COOH 2 ml, CH₂Cl₂ 2 ml, H₂O 0.1 ml, O₂ 1 atm, Zn powder 1.0 g.

^b Adamantane (0.05 g) dissolved in CH₂Cl₂ (1 ml).

^c cy-C₆H₁₂ (0.5 ml) + cy-C₆D₁₂ (0.5 ml).

^d Measured from the areas (a.u.) of m/z (57) for cy-C₆H₁₁OH, m/e (61) for cy-C₆D₁₁OH, m/z (55) for cy-C₆H₁₀O, m/z (58) for cy-C₆D₁₀O.

system (1:13:88) < metal-porphyrin system (1:25:250).

Kinetic isotope effect for the oxidation of cyclohexane using a mixture of cy-C₆D₁₂ and cy-C₆H₁₂ was measured by GC-MS [2]. The large kinetic isotope effect on the conversion rate of cyclohexane was observed (k_H/k_D = 3.6). This result suggests that the cleavage of C-H bond of cyclohexane is the rate determining step in the oxidation (step 2 in Scheme 1). The isotope effect (3.6) observed in our reaction system was larger than that in the free HO· system (1.2) [2,4], Gif(IV) system (2.5) [2,3] and SmCl₃/Gr cathode (1.7) [2], and smaller than that in the metal-porphyrin system (~5) [2,5].

From the results described above, the reactivity of the active oxygen generated in SmCl₃-catalytic system is different from those of free HO· system [4], Fe^V=O (Gif-Orsay-Texas [3]), and Por·⁺Fe^{IV}=O (metal-porphyrin [5]), and is not similar to the active oxygen on SmCl₃/Gr cathode [2]. The oxidation state of samarium during the oxidation may be a trivalent state, because the redox potential of Sm³⁺/Sm²⁺ (-1.55 V vs. RHE) is lower than that of Zn²⁺/Zn⁰ (-0.76 V vs. RHE). Moreover we have observed that LaCl₃, which can not be reduced to the divalent state, exhibits good catalytic activity for the oxidation [1]. Differences in TON using different carbox-

ylic acids can be explained in terms of the steric hindrance effect between carboxylic groups coordinated on Sm³⁺ and cyclohexane during the oxidation. The favorable effect of H₂O addition on the increase in TON for the oxidation of cyclohexane may be ascribed to the promotion of the transfer of e⁻ from Zn and that of H⁺ from CH₃COOH to the O₂ coordinated on Sm³⁺ active species. Although an exact form of Sm³⁺ species cannot be defined at this moment.

Further investigations are needed to clarify the real active form of Sm³⁺ species, the nature of the active oxygen in SmCl₃-catalytic system, and to explain the difference between this oxygen and the active oxygen on SmCl₃/Gr cathode.

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