



Oxidation of adamantane with O₂ catalysed by VO(acac)₂ and reactivity of active species in acetic acid

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ABSTRACT

The oxidation of adamantane (470 mM) catalysed by VO(acac)₂ (0.5 mM) with 1 atm O₂ in acetic acid at 393 K was studied. The major product was 1-adamantanol, and minor ones were 2-adamantanol and 2-adamantanone. The selectivity for 1-adamantanol (3°-selectivity) was almost constant at 75% under all oxidation conditions. The VO(acac)₂ catalyst functioned efficiently in the oxidation with a turnover number (TON) of 440 over 600 min. The oxidation rate of adamantane was enhanced by 5.5 times by the addition of CF₃SO₃H (2.2 mM) to acetic acid. Reactivities of various alkanes in the presence of VO(acac)₂ catalyst and product selectivities indicated the contribution of electrophilic active species in the oxidation. The rate-determining step was dissociation of the C–H bond of alkane by electrophilic active V species. The activity of the VO(acac)₂ catalyst is significantly different from the autoxidation promoter, Co(acac)₃. A reaction scheme for the oxidation is proposed on the basis of the reactivities and UV–vis and ESR spectroscopic studies.

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1. Introduction

Adamantane oxygenates are essential materials in photoresists that are exposed to ArF excimer laser light and in medicines for Parkinson's disease, and anticancer and antiviral treatment [1–3]. They are mainly manufactured by the sulphuric acid oxidation with a large amount of pitch and SO₂ as by-products [4]; therefore, development of selective and catalytic oxidation of adamantane under mild conditions is an attractive subject for green and sustainable chemistry.

Over the last few decades, various oxidation catalysts working under mild conditions using H₂O₂ [5–18] and a gaseous mixture of O₂ and H₂ [19–25] have been reported. These oxidants are more environmental friendly than heavy metal oxides, H₂SO₄ and organic peroxides; however H₂O₂ is expensive for bulk chemical synthesis and a gaseous mixture of O₂ and H₂ can explode. The most attractive and economical oxidant is O₂. The ultimate catalytic oxidation system would be air (P(O₂) 0.21 atm) without any reducing agents under mild conditions. Several oxidation catalysts working under mild conditions have been reported; e.g. ruthenium complexes [26–30], polyoxometalates [27–32], N-hydroxy imide [33],

and V/montmorillonite catalysts [34]. These catalytic oxidation systems have some drawbacks such as a high cost of catalysts and a low formation rate of products. We have recently reported a simple vanadium catalyst for alkane oxidation working with O₂ (≤1 atm) in acetic acid [35], whose activity for oxidation of cyclohexane was higher than that of autoxidation promoters such as cobalt and iron complexes. Adamantane has also been oxidised by a vanadium catalyst. In this study, we describe the oxidation of adamantane with a vanadium catalyst.

2. Experimental

Oxidation of adamantane was carried out in a Pyrex flask (100 mL) with a condenser, a gas introduction tube and a thermocouple. VO(acac)₂ catalyst (0.5 mM) was dissolved in a mixture of adamantane (0.47 M) and acetic acid (10 mL) in the flask. The temperature of the flask was controlled by using an oil-bath and the real reaction temperature was monitored with a thermocouple. Oxidation was started by stirring with a magnetic-spin bar, bubbling O₂ (10 mL min⁻¹) into the solutions and continued for 360 min. The products in the gas phase were analysed each hour by GC (Shimadzu GC-8A, TCD-detector) with a Poropak Q packed column (40 × 2 m). After the oxidation, the reaction solutions were neutralised with NaOH (aq.), and the products were extracted with a CH₂Cl₂/n-C₇H₁₆ or 1-C₄H₉OH/n-C₇H₁₆ mixture. The extracted

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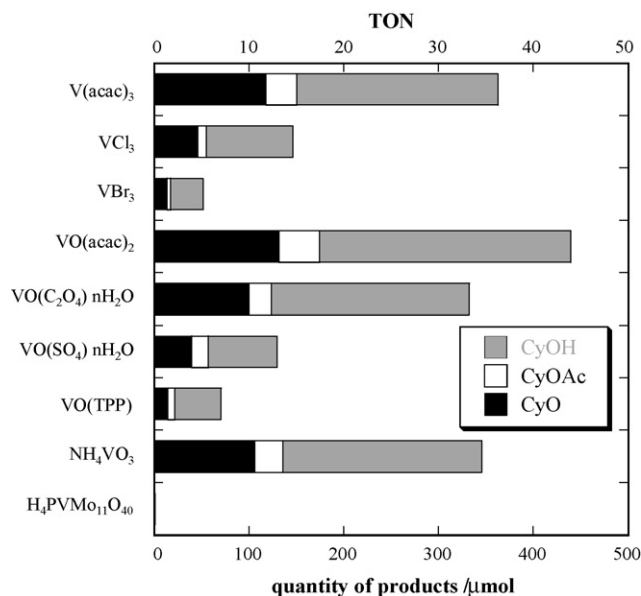


Fig. 1. Oxidation of cyclohexane with 1 atm O_2 by vanadium catalysts for 360 min at 365 K. Catalyst 0.5 mM (10 μ mol), *cy*- C_6H_{12} 1.85 M (4 mL), AcOH 16 mL.

reaction mixture was analysed by GC (Shimadzu GC-14A, FID-detector) and GC-MS (Shimadzu QP-2000A) with an HR-20M capillary column (0.25 \times 25 m) using naphthalene as an external standard. All reagents were special grade and used without further purification.

To obtain information on their active species and the oxidation state of vanadium, UV-vis spectroscopy studies were performed on the reaction mixture at 365 K with a JASCO V-650 spectrometer and electron spin resonance (ESR) spectra studies were performed on the mixture at room temperature with a JEOL JES-FA100 (X-band) spectrometer. Mn^{2+}/MgO was used as an external standard.

3. Results and discussion

3.1. Screening of V catalysts in oxidation of cyclohexane

We have recently communicated that vanadium compounds are active for the oxidation of cyclohexane with O_2 in AcOH solvent [35]. Fig. 1 shows the details of the oxidation of cyclohexane catalysed by various vanadium catalysts. The products were cyclohexanol (CyOH), cyclohexanone (CyO), cyclohexyl acetate (CyOAc), and CO_2 from acetic acid. $VO(acac)_2$, $V(acac)_3$, NH_4VO_3 , and $VO(C_2O_4)$ catalysts showed similar yields of products and similar product distributions; however their own oxidation states were different, V^{4+} , V^{3+} , V^{5+} , and V^{4+} , respectively. These data indicate that common active vanadium species should form during the oxidation. Other vanadium catalysts, VCl_3 , VBr_3 , $VO(SO_4)$, and $VO(TPP)$, showed low oxidation activities, except for $H_4PVMo_{11}O_{40}$. Counter-anion species may affect the generation of active vanadium species.

Table 1
Oxidation of adamantane with 1 atm O_2 by $VO(acac)_2$ catalyst^a

Adamantane (mM)	Concentration of products (mM) (yield, %)					3°-selectivity (%)	$r(CO_2)$ (mmol h ⁻¹)
	1-AdOX	2-AdOX	2-AdO	1,3-AdOX	Total		
99	9.9 (10.0)	1.6 (1.6)	2.0 (0.2)	n.d. ^b (-)	13.5 (13.6)	74	0.0127
190	33.1 (17.4)	4.6 (2.4)	6.5 (3.4)	1.2 (0.6)	45.5 (23.9)	75	0.0377
470	113 (24.0)	15.3 (3.2)	20.6 (4.4)	12.9 (2.7)	161 (34.2)	76	0.0870
890	179 (20.1)	27.8 (3.1)	31.1 (3.5)	22.6 (2.5)	261 (29.3)	75	0.167

^a $T=393$ K, $VO(acac)_2$ 0.5 mM (5 μ mol), AcOH 10 mL, $P(O_2)$ 1 atm, reaction time 6 h.

^b not detected.

$VO(acac)_2$ catalyst showed the highest oxidation activity and good reproducibility among the vanadium compounds tested; therefore, oxidation of adamantane by the $VO(acac)_2$ catalyst in AcOH was studied.

3.2. Oxidation of adamantane by $VO(acac)_2$ catalyst

Table 1 shows the oxidation activity of $VO(acac)_2$ catalyst for oxidation of adamantane as a function of adamantane concentration. The major product was 1-adamantanol with 2 mol% detected as acetic acid 1-adamantyl ester. The sum of these two is indicated as 1-AdOX (X: -H or $-C(O)CH_3$). Other products were 2-adamantanol and its acetate (2-AdOX), 2-adamantanone (2-AdO), 1,3-adamantanediol and its acetates (1,3-AdOX) and CO_2 from AcOH solvent. Trace quantities of 1,4-adamantanediol and 5-hydroxy-2-adamantanone were also produced.

The concentrations of the products increased with increasing concentrations of adamantane from 99 to 890 mM. The highest concentration for the sum of adamantane oxygenates (261 mM) was obtained at 890 mM of adamantane, and the turnover number (TON) based on vanadium was 522. A TON in 1 h was defined as a turnover rate. The highest turnover rate of 87 h⁻¹ in this work is much higher than these of previous reports; e.g. 4.9 h⁻¹ for $\{[WZnRu_2(OH)(H_2O)](ZnW_9O_{34})_2\}^{11-}$ [27], 2.4 h⁻¹ for $H_5PV_2Mo_{10}O_{40}$ [32], 2.2 h⁻¹ for $NHPI-Co(acac)_2$ [33], and 1.6 h⁻¹ *V*-montmorillonite [34]. The $VO(acac)_2$ catalyst functioned efficiently in the oxidation. However, the sum of yields of adamantane oxygenates showed a maximum of 34% at 470 mM of adamantane. The highest concentration of adamantane (890 mM) is close to its saturation concentration and a white deposition of adamantane was observed on the wall of flask during the oxidation. Near saturation concentrations of adamantane are not favourable for effective oxidation. A parameter of 3°-selectivity was defined as Eq. (1), the sum of 3°-oxygenated product yields per the sum of mono-oxygenated product yields. The 3°-selectivities were almost constant at 75% in all concentrations of adamantane, as shown in Table 1. The characteristics of active species are not dependent on the concentrations of adamantane.

$$3^\circ\text{-selectivity} = \frac{1\text{-AdOX}}{1\text{-AdOX} + 2\text{-AdO} + 2\text{-AdOX}} \quad (1)$$

Fig. 2 shows the time courses of the oxidation of adamantane (470 mM) for 600 min. The sum of the quantities of adamantane oxygenates increased showing a weak sigmoidal curve with reaction time. The time courses of formation of each oxygenates also showed weak sigmoidal curves except for 1,3-AdOX. This observation indicates the successive formation of 1,3-AdOX from 1- or 2-AdOX; therefore, oxidation of 1-AdOH by the $VO(acac)_2$ catalyst was studied in a separate experiment. Formation of 1,3-AdOX was confirmed in the oxidation of 1-AdOH, whereas 2-AdOH was oxidised to 2-AdO. 1,3-AdOX was produced by successive oxidation of 1-AdOH. The TON of vanadium for the sum of quantities of products was higher than 440 TON (44% yield) at 600 min. The 3°-selectivities were almost constant at 75% without dependence on

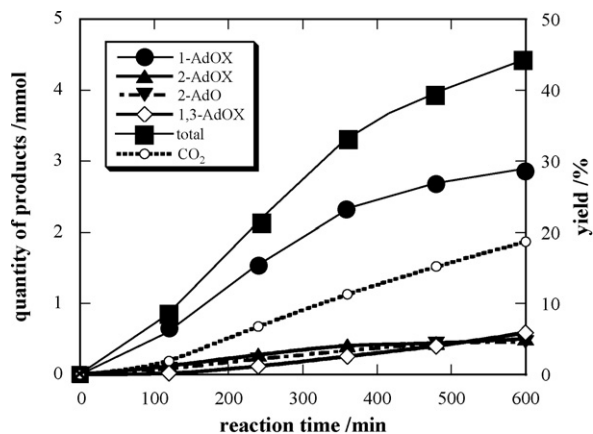


Fig. 2. Time courses of the oxidation of adamantane with 1 atm O₂ by VO(acac)₂ catalyst. *T* = 393 K, VO(acac)₂ 0.5 mM (10 μmol), adamantane 470 mM (10 mmol), AcOH 20 mL.

reaction time. These facts indicate that oxidation of adamantane by the VO(acac)₂ catalyst with O₂ in acetic acid proceeded steadily.

Fig. 3a shows the dependence of formation rates of products, averaged over 360 min, on reaction temperatures. Each formation rate increased exponentially from 338 to 393 K. The major product was 1-AdOX and the product distributions were similar at all reaction temperatures. The oxidation rate of adamantane (*r*, mol L⁻¹ h⁻¹) calculated from the sum of the formation rates of adamantane oxygenates increased exponentially with reaction

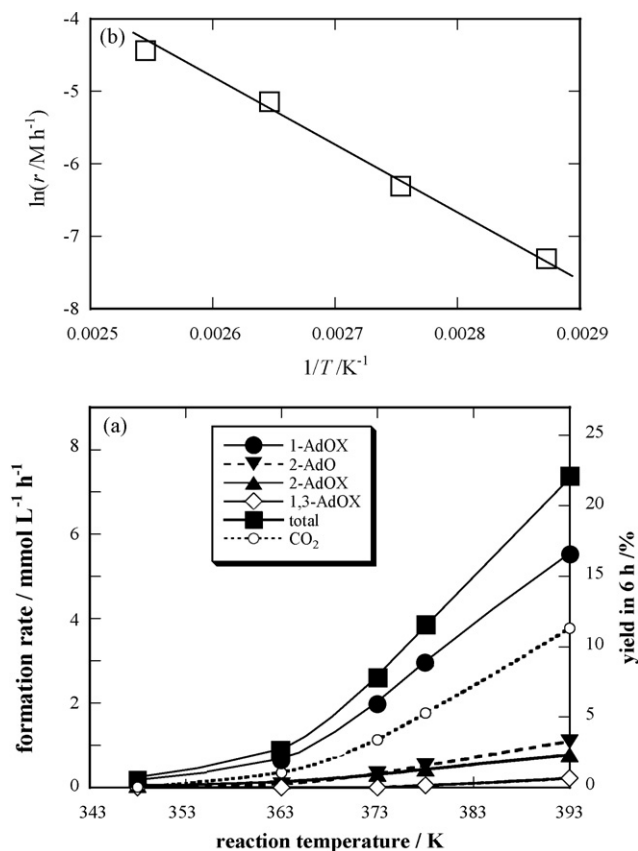


Fig. 3. Reaction temperature (*T*) dependence on the formation rate of products (*r*) in the oxidation of adamantane with 1 atm O₂ by VO(acac)₂ catalyst (a), and a plot of ln *r* against 1/*T* (b). VO(acac)₂ 0.5 mM (5 μmol), adamantane 190 mM (2 mmol), AcOH 10 mL.

temperatures (*T*). A plot of ln *r* against 1/*T* is shown in Fig. 3b, which had a good linearity. The apparent activation energy was 76 kJ mol⁻¹. This value is higher than that of <20 kJ mol⁻¹ for the diffusion process of reactants and products and the rate-determining step in the oxidation is the chemical reaction.

When air (*P*(O₂) = 0.2 atm) was used for the oxidation of adamantane, selective oxygenation of adamantane proceeded with a good yield of 12% (120 TON) in 6 h. The 3°-selectivity was 76%, very similar to the 75% obtained at *P*(O₂) = 1 atm. This result indicated the possibility of aerobic oxidation of adamantane to oxygenates by the VO(acac)₂ catalyst.

The 3°-selectivity of 75% was always constant for the oxidation of adamantane under all reaction conditions. When the 3°-selectivity value was estimated by using the reactivity of the C–H bond defined as each oxygenate yield per number of C–H bonds, the ratio of the reactivity of 2° and 3° C–H bonds was 1:9; i.e. the 3° C–H bond was 9 times more reactive than the 2° C–H bond. The active vanadium species may be electrophilic because the electron density of 3° C–H bond is higher than that of 2° C–H bond. If this is the case, the oxidation rate of adamantane with electrophilic active species would be accelerated by addition of an electron-withdrawing ligand to AcOH solvent; therefore, trifluoromethanesulphonic acid (HOTf) (2.2 mM) was added to AcOH solvent, and an acceleration of the oxidation rate of adamantane (99 mM) was observed at 365 K. The TON of the sum of quantities of products was increased from 2.0 h⁻¹ in AcOH solvent to 13 h⁻¹ in a mixed solvent of HOTf and AcOH. A blank test was performed for the oxidation of adamantane without VO(acac)₂ catalyst, which was not enhanced by addition of HOTf. The 3°-selectivity decreased slightly from 75% in AcOH to 68% in the mixed solvent. These results indicate that the catalytic activity of VO(acac)₂ was enhanced by using the mixed solvent of HOTf and AcOH and that the nature of the active oxygen species was not influenced strongly.

3.3. Reactivities of active V species

As described above, active vanadium species may be electrophilic in the oxidation of adamantane. To obtain more information on the characteristics of active vanadium species [36], the activity of vanadium species for various oxidations was studied and compared with that observed for a typical autoxidation promoter Co(acac)₃, as shown in Table 2. Reaction time was controlled to be as short as possible (TON = 2–5) to inhibit successive oxidation of the initial products.

3.3.1. Ratio of alcohol and ketone (A/K)

Initial ratios of alcohol to ketone yields Eq. (2) were studied for oxidation of cyclohexane at the beginning of the oxidation at 365 K.

$$A/K = \frac{\text{CyOH} + \text{CyOAc}}{\text{CyO}} \quad (2)$$

The A/K ratio was 5.2 with the VO(acac)₂ catalyst and was 1.0 with the Co(acac)₃ promoter. It has been reported that the A/K ratio

Table 2
Characters of VO(acac)₂ catalyst and Co(acac)₃ promoter in various oxidations^a

Reactant	Parameter	VO(acac) ₂ catalyst	Co(acac) ₃ promoter
cy-C ₆ H ₁₂	A/K	5.2	1.0
cy-C ₆ H ₁₂ /cy-C ₆ D ₁₂	k _H /k _D	2.8	7.0
cy-C ₅ H ₁₀ /cy-C ₆ H ₁₂ ^b	C ₅ /C ₆	0.44	0.65
cis-Me ₂ CyH ^c	RC	37%	20%
trans-Me ₂ CyH ^c	RC	31%	12%

^a *T* = 365 K, AcOH (80 vol%), catalyst or promoter 0.5 mM.

^b *T* = 352 K.

^c *cis*- or *trans*-1,2-dimethylcyclohexane.

was 1 for typical autoxidation reactions [37,38]. The A/K ratios indicate that the oxidation by VO(acac)₂ catalysts is different from the autoxidation.

3.3.2. Kinetic isotope effect (KIE)

Kinetic isotope effects were studied for competitive oxidation of cyclohexane (cy-C₆H₁₂) and deuterated cyclohexane (cy-C₆D₁₂) (1:1 (mol)) at 365 K. Major products were cy-C₆H₁₁OH and cy-C₆D₁₁OH, and minor ones were cy-C₆H₁₀O, cy-C₆D₁₀O, cy-C₆H₁₁OC(O)CH₃ and cy-C₆D₁₁OC(O)CH₃. These products were identified by GC-MS. A KIE value was calculated from the sum of quantities of oxygenated cy-C₆H₁₂ and the sum of quantities of oxygenated cy-C₆D₁₂ Eq. (3).

$$\text{KIE} = \frac{\text{sum of oxygenated cy-C}_6\text{H}_{12}}{\text{sum of oxygenated cy-C}_6\text{D}_{12}} \quad (3)$$

A significant KIE value of 2.8 was obtained for oxidation by the VO(acac)₂ catalyst. This KIE value was as large as that observed for the stoichiometric oxidation of cyclohexane with VO(O₂)(Pic)·2H₂O [39]. These facts indicated that the rate-determining step was dissociation of the C–H bond of cyclohexane. On the other hand, a larger KIE value of 7.0 was observed with the Co(acac)₃ promoter and was reasonable as the autoxidation mechanism concerned the alkylperoxy radical (ROO·) or the alkoxy radical (RO·) for cleavage of the C–H bond [40,41].

3.3.3. Reactivity of cyclohexane and cyclopentane (C₅/C₆ parameter)

The competitive oxidation of cyclohexane and cyclopentane was studied to obtain the reactivity of active species. The products were cyclohexanol, cyclohexyl acetate, cyclohexanone, cyclopentanol, cyclopentyl acetate, cyclopentanone and CO₂. A parameter, C₅/C₆, was defined as the relative oxidation reactivity of cyclopentane to cyclohexane per number of C–H bonds Eq. (4).

$$C_5/C_6 = \frac{\text{cyclopentane oxygenates yield}/5}{\text{cyclohexane oxygenates yield}/6} \quad (4)$$

This parameter reflects the character of the active oxygen species and the mechanism of dissociation of a C–H bond, hydride abstraction (1 < C₅/C₆), hydrogen radical abstraction (0.6 ≤ C₅/C₆ ≤ 1), and electrophilic attack on a C–H bond (C₅/C₆ < 0.5) [9,42]. A C₅/C₆ factor of 0.44 was obtained for the oxidation by the VO(acac)₂ catalyst and that of 0.65 was obtained for oxidation with the Co(acac)₃ promoter. These results indicate the electrophilicity of active oxygen species generated from the VO(acac)₂ catalyst and radical species generated from the Co(acac)₃ promoter, respectively.

3.3.4. Retention of configuration (RC parameter)

Retention of configuration on the tertiary C–H bond for the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane (*cis*-, *trans*-Me₂CyH) with 0.5 atm of O₂ was studied to obtain information on intermediates formed during the oxidation. The major products were *cis*- and *trans*-1,2-dimethylcyclohexane-1-ol (*cis*- and *trans*-Me₂CyOH). Minor products were *cis*- or *trans*-1,2-dimethylcyclohexane-3-ol, -4-ol, -3-one, -4-one, and *cis*- or *trans*-1-formyl-2-methylcyclohexane. The configurations of the two methyl groups of the minor products were retained completely. The retention of configuration (RC) parameter was defined as Eq. (5).

$$\text{RC} = \frac{|\text{(yield of } cis\text{-Me}_2\text{Cy-1-OH)} - \text{(yield of } trans\text{-Me}_2\text{Cy-1-OH)}|}{\text{sum yield of Me}_2\text{Cy-1-OH}} \quad (5)$$

RC values were 37% and 31%, respectively, for oxidation of *cis*-Me₂CyH and *trans*-Me₂CyH by the VO(acac)₂ catalyst. It is considered that an alkyl radical intermediate should form in both electrophilic and radical reactions [13,37,43] and its stereochemistry on tertiary carbon may change by subsequent addition of a functional group. The rate constant for disappearance of stereochemistry of the tertiary alkyl radical is estimated at about 10⁹ s⁻¹ (first-order kinetics) at 365 K [44]. If the addition of a functional group to the alkyl radical intermediate was very fast (<<10⁻⁹ s), the stereochemistry was retained and a higher RC value was observed. If the addition of a functional group was slow (>>10⁻⁹ s), a mixture of *cis*- and *trans*-Me₂Cy-1-OH was produced and a lower RC value was observed [45].

When P(O₂) was decreased to 0.2 atm, the RC value was 39% for the oxidation of *cis*-Me₂CyH. RC values were not affected by P(O₂). RC values for the oxidation of *cis*-Me₂CyH and of *trans*-Me₂CyH by the Co promoter were 20% and 12%, respectively. These values were lower than those by the VO(acac)₂ catalyst. The life time of the alkyl intermediate in oxidation by the VO(acac)₂ catalyst may be shorter than that in the autoxidation by the Co promoter. The kinetic constant of O₂ addition to the alkyl radical was reported as k = 10⁹–10¹⁰ L mol⁻¹ s⁻¹ [46,47]. These results indicate that the vanadium active species dissociate a C–H bond of adamantane (alkane) and immediately stabilize the alkyl radical intermediate to the oxygenated product through a rebound-like mechanism [13,48].

3.4. Spectroscopic studies of intermediates

To obtain information on the oxidation state of vanadium and the active oxygen species, *in situ* UV–vis and ESR spectra of the reaction mixture were studied, and the results are shown in Figs. 4 and 5, respectively. Cyclohexane was used instead of adamantane because deposition of adamantane on the wall of the optical cell was a disadvantage for spectroscopic studies. In Fig. 4, the UV–vis spectrum (i) is for solutions of VO(acac)₂ 0.5 mM, cyclohexane 1.85 M and AcOH (sample 1), spectrum (ii) is for oxidation solutions of sample 1 with O₂ for 3 h (sample 2), and spectrum (iii) is for solutions of sample 2 after passing Ar over it (sample 3) in a standard UV-cell (optical length 10 mm). Strong absorption at wavelength lower

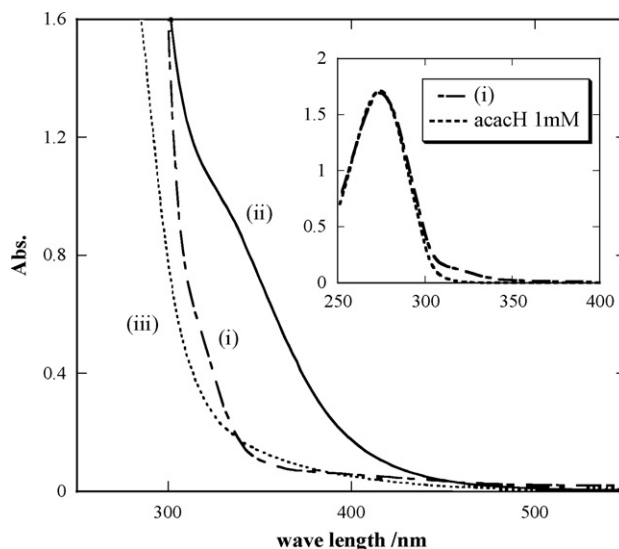


Fig. 4. UV–vis spectra of the reaction mixture (i) before and (ii) after oxidation 3 h, and (iii) after Ar purge for 0.3 h, T = 365 K, VO(acac)₂ 0.5 mM, AcOH 8 ml, cy-C₆H₁₂ 1.85 M, (i and iii) P(Ar) 1 atm, (ii) P(O₂) 1 atm. Optical length: 10 mm (2 mm for inset).

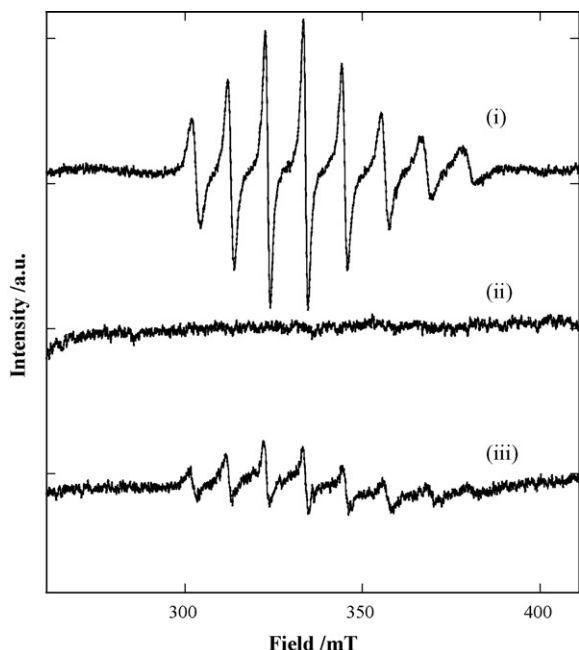
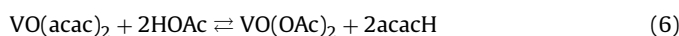


Fig. 5. ESR spectra of the reaction mixture (i) before and (ii) after oxidation for 3 h, and (iii) after Ar purge for 0.3 h. Oxidation conditions: $T = 365$ K, $\text{VO}(\text{acac})_2$ 0.5 mM, C_6H_{12} 1.85 M, AcOH 16 mL. ESR measurement conditions: $T = 298$ K, (i and iii) $P(\text{Ar})$ 1 atm, (ii) $P(\text{O}_2)$ 1 atm.

than 300 nm was observed in spectrum (i); therefore, the UV–vis spectrum of sample 1 was measured by a shorter UV cell (optical length 2 mm), as shown in the inset of Fig. 4. The absorption peak at 274 nm for the sample 1 was identified as the absorption of acetylacetone (acacH) and corresponded to that of solutions of 1 mM acacH in AcOH. This result indicates that all acac^- ligands of $\text{VO}(\text{acac})_2$ exist as acacH in AcOH Eq. (6). $\text{VO}(\text{acac})_2$ is present as $\text{VO}(\text{OAc})_2$ under reaction conditions.

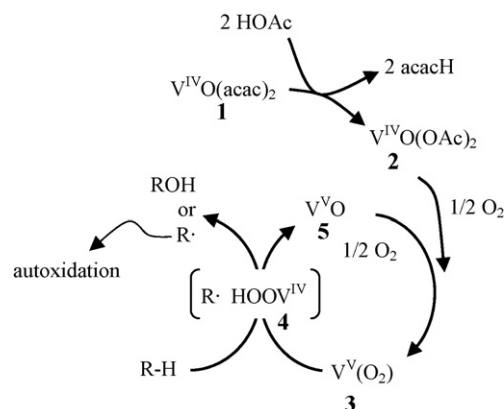


A new broad UV absorption at 300–400 nm was observed in spectrum (ii) of the oxidation solutions (sample 2). This broad UV absorption disappeared by passing Ar over sample 2 for 0.3 h to produce sample 3 (Fig. 4(iii)), but reappeared after oxidation of sample 3; therefore, reversible chemical species caused the absorption at 300–400 nm.

ESR spectra of sample 1 showed eight typical signals of V^{4+} at room temperature in Ar (Fig. 5(i)) [49]. The g -factor was calculated as 1.971 and A was 109 G. No ESR signal was observed for sample 2 (Fig. 5(ii)). This result indicated that the V^{4+} (d^1 state) was oxidised to V^{5+} (d^0 state) during the oxidation. On the other hand, weak ESR signals assigned to V^{4+} were observed for sample 3 (Fig. 5(iii)). It is considered that vanadium species mainly existed as V^{5+} . It has been reported that vanadium peroxide species show a broad UV absorption from 300 to 400 nm, which is assigned to charge transfer from peroxide to vanadium [50]. The species that showed broad UV absorption from 300 to 400 nm in Fig. 4(ii) may be V^{5+} peroxide as similar to $\text{V}^{\text{V}}\text{O}(\text{O}_2)(\text{OAc})$.

3.5. Reaction scheme

A reaction scheme for the oxidation of adamantane estimated from all of the experimental results is proposed in Scheme 1. The starting form of $\text{V}^{\text{IV}}\text{O}(\text{acac})_2$ (1) catalyst is converted to $\text{V}^{\text{IV}}\text{O}(\text{OAc})_2$ (2) by a ligand exchange reaction with AcOH, as shown in Fig. 4. The species 2 (V^{IV}) is oxidised to V^{V} species ($\text{V}^{\text{V}}(\text{O}_2)$ (3)) under the



Scheme 1. Oxidation mechanisms in the $\text{VO}(\text{acac})_2/\text{AcOH}$ catalytic system.

oxidation conditions. This species 3 shows a broad UV–vis absorption at 300–400 nm and was electrophilic. The species 3 attacks C–H bonds of adamantane and dissociates a C–H bond forming an alkyl radical intermediate (R^{\cdot} HOOV(4)). The intermediate species 4 immediately produces alcohol and $\text{V}^{\text{V}}\text{O}$ (5) through a rebound-like mechanism, as described by the C_5/C_6 parameter. The dissociation of a C–H bond is the rate-determining step ($\text{KIE} = 2.8$) during the oxidation. The reaction rate between the species 3 and adamantane is accelerated in a mixed solvent of HOTf and AcOH. The oxidation reactivity of the 3 species may be enhanced by coordination of ^-OTf . The inner sphere alkyl radical intermediate occasionally leads to the outer sphere. Leaked alkyl radical from the species 4 may initiate autoxidation. Oxidation of adamantane (alkanes) proceeded with electrophilic active V species but the autoxidation path may contribute partly. The species 5 regenerates the species 3 by oxidation with O_2 .

4. Conclusion

The simple vanadium catalyst, $\text{VO}(\text{acac})_2$, showed good oxidation activity of adamantane to the adamantane oxygenates with 1 atm O_2 and at 393 K. The 3° -selectivities were always constant at 75% in all of the reaction conditions in this work. The highest TON of vanadium was 440 over 600 min and a good yield of 44% was obtained. UV–vis and ESR spectroscopic studies indicated that the active species may be the $\text{V}^{\text{V}}(\text{O}_2)$ species. Reactivities and selectivities under various oxidations of alkanes indicated that the vanadium active species was electrophilic in the oxidations. The rate-determining step in the oxidation was dissociation of a C–H bond of alkane, and the vanadium active species functioned in the oxidation while retaining its oxidation state of 5+. The oxidation system by vanadium catalyst with O_2 may be one of the candidates for the adamantane oxidation process, if product selectivities can be improved.

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