

Homogeneous green catalyst for epoxidation of cyclooctene by mono oxovanadium(IV) complexes of N₂O₂ donate ligand system

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Abstract

A significant effort has been done towards the development of new catalysts for the synthesis of epoxides in a more environmental friendly way. We have found that the mono oxovanadium(IV) complexes of the N₂O₂ donor set ligands are able to catalyze selective epoxidation of cyclooctene with high yield using O₂ in polar solvents. In general, catalytic activity increases by decreases of the number of electron – donating groups and the catalytic selectivity varies according to the types of substituents in the ligands. The vanadium complexes with strongly donor ligands, are more stable during the oxidation process. The conversion of cyclooctene increases with the $E_{\text{redox}}^{\text{O}^{\cdot}}/\Delta E_{\text{p}}$ ratio of V⁵⁺/V⁴⁺ couples.
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1. Introduction

Effective and selective methods for the catalytic functionalization of hydrocarbons are a major challenge in both synthetic and industrial chemistry [1–3]. Development in this area is based on different strategies with the aim of designing selective, stable, and high turnover catalytic systems. These strategies involve using of efficient and clean oxidants. In particular, the selective transformations of alkenes to oxygen-containing compounds such as alcohols, ketones and carboxylic acids with molecular oxygen are very important reactions for the chemical worldwide industry [4]. The importance of utilization of molecular oxygen as an oxidant is driven by its abundance and by its potential to be a more environmental friendly oxidant, which results in no-waste technology [5].

Homogeneous liquid-phase oxidation of hydrocarbons using molecular oxygen as an oxidant is commonly referred to auto-oxidation. Now we propose a new example of auto-oxidation using a transition metal-catalyzed aerobic oxidation [6].

More recently, vanadium(IV) co-ordination compounds have been shown to catalyze selective oxidation of alkenes by molecular oxygen [7,8]. The catalyst systems employed were monomeric oxovanadium complexes of Schiff bases [9], such as Schiff bases derived from salicylaldehydes and 1,2-diaminoalkanes, or mixtures of vanadyl acetylacetonate and Schiff bases containing amine constituents [10,11].

The present article describes our recent work on the aerobic oxidation of cyclooctene by O₂, using oxovanadium(IV) mixed donor Schiff base complexes as catalysts.

2. Experimental

2.1. Physical measurements

Infrared spectra were recorded as KBr pellets using Unicam Matson 1000 FT-IR, ¹H NMR and ¹³C NMR spectra by a Bruker FT NMR 500 (500 MHz) spectrophotometer using TMS as internal standard and CDCl₃ and (CD₃)₂SO as solvent. Elemental analyses (C, H, N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analyses system KBr pellets, GmbH, West Germany). Melting points were determined on a BUCHI Melting point B-540. The products were identified by GC with a CHROMPACK CP 9001 gas chromatograph, and compared with retention times of authentic samples. The

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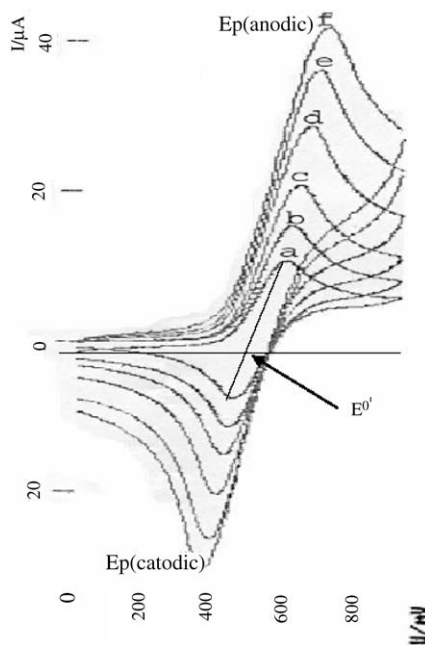


Fig. 1. Cyclic voltammogram of VOL² in different scan rates (a) 20 mV/S, (b) 50 mV/S, (c) 100 mV/S, (d) 200 mV/S, (e) 300 mV/S, (f) 500 mV/S at 25 °C under argon with 0.1 M TBAH as the supporting electrolyte in acetonitrile.

GC–MS system consists of a GC HP 6890 series instrument and a MS HP 5973 MSD instrument. Cyclic voltammetry was performed using a Bio-analytical system. The working, auxiliary, and reference electrodes were glassy carbon, platinum wire, and AgCl/Ag, respectively. Electrochemical measurements were performed at room temperature (25 °C) under argon with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte by EG & G potentiostat / galvanostat 273 A. ΔE_p (mV) is equal to $E_p(\text{cathodic}) - E_p(\text{anodic})$ and $E^{0'}$ is obtained from crossing of a line that link $E(\text{anodic})$ and $E(\text{cathodic})$ over the potential axis (mV) in the cyclic voltammogram as shown in Fig. 1.

2.2. Materials

Oxygen gas was passed through a calcium chloride drying tube before admission to the reaction system. Cyclooctene was distilled under nitrogen and treated with activated alumina to remove alkyl hydro peroxide and impurities, and stored in a refrigerator. A 1,2-propylene diamine, 2-hydroxy benzaldehyde, 2-hydroxy acetophenone, 2',4'-dihydroxy acetophenone, and vanadyl acetylacetonate were used as received from commercial suppliers. Solvents (ethanol, ether, methanol, and acetonitrile) were dried and distilled by standard methods before using. DMF and DMSO were used without further purification.

Solvents for electrochemical experiments were re-distilled and passed through a column of activated alumina.

The Schiff bases ligands, H_2A^x ($x = 1-6$), and their vanadyl complexes, VOA^x ($x = 1-6$), were prepared under ambient conditions according to our recent procedure [12]. Ligands were obtained by condensation of the half units and the appropriate aldehyde or ketones. Half units were also synthesized by mono

condensation of the 1,2-propane diamine and appropriate aldehyde or ketones.

2.3. Catalytic oxidations

Catalytic oxidation was performed in stirred flasks. All glassware was oven-dried prior to use. In a typical experiment 5 μmol of the vanadyl complexes were dissolved in freshly distilled acetonitrile (15 ml, for VOL¹, VOL², VOL⁴, VOL⁵) or the mixed solvent of acetonitrile and DMF in 3:2 ratio (25 ml, for VOL³ and VOL⁶) at 40 °C. The system was evacuated and purged with argon gas. After saturation of the solution with dioxygen, 50 mmol of freshly distilled cyclooctene was injected. The reactions were carried out at 75–78 °C for 24 h under 1 atm of O₂ that was continuously replenished. The reaction products were monitored at periodic time intervals, using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC) and by GC–MS coupling.

In this procedure, precise measured quantify of internal standard acetophenone, is introduced into each sample after quenching with P(Ph)₃ and the ratio of analyt peak area to internal standard peak area is the analytical parameter. The selectivity of the reaction for the different products were calculated on the basis of the three major products which represent almost 90% of all products which obtained, since other oxygenated minor products are formed.

3. Results and discussion

The oxovanadium(IV) complexes with tetradentate Schiff base ligands that were used in this study are shown in Fig. 2. They were prepared as previously described [12].

They are remarkably stable to air, water and heat. In addition one of the tetradentate oxovanadium(IV) complex (VOL³) is orange. It shows a vibration ν ($V=O$) at 884 cm^{-1} that specifies polymeric form, while the five other monomeric forms are green and their vibrations are around 970 cm^{-1} (938–1000 cm^{-1}) [13,14].

The vanadyl salen complexes (VOL^x, $x = 1-6$) were tested as catalyst for aerobic oxidation of cyclooctene. Typical catalytic reaction conditions involving cyclooctene, catalyst and solvent (acetonitrile or mixture of acetonitrile and DMF, 3:2 ratio) at elevated temperatures (75–78 °C). The reaction medium was homogeneous liquid-phase except for VOL³ catalyst that is insoluble in the reaction media. Stirring was continued under 1 atm of O₂ while oxygen was continuously replenished; periodic product sampling was conducted. Under these conditions, cyclooctene

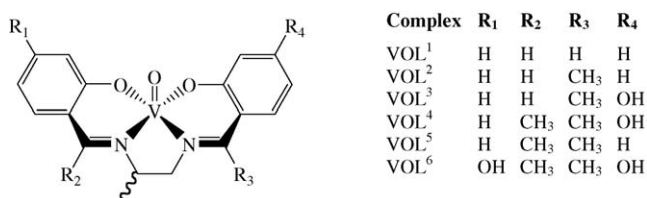


Fig. 2. General structure of oxovanadium(IV) complexes.

Table 1
Catalytic epoxidation of cyclooctene by O₂ at 75–78 °C and formal potentials for redox vanadium (V/IV) couples^a

Complex	E_{redox}^0 (mV), (ΔE_p , mV) ^b	$E_{\text{redox}}^0/\Delta E_p$	Average TOF (h ⁻¹), (% conversion)	% Identified products ^c		
				Epoxide	Alcohol	Ketone
VOL ¹	508 (66)	7.7	333 (80)	37	43	19
VOL ²	501.5 (66)	7.6	279 (67)	60	29	11
VOL ³	Insoluble	Insoluble	104 (25)	49	35	16
VOL ⁴	484.5 (62)	7.81	379 (91)	58	28	14
VOL ⁵	480 (70)	6.85	241 (58)	41	34	25
VOL ⁶	475 (70)	6.8	154 (37)	30	47	23

^a Catalytic oxidation by VOL¹, VOL², VOL⁴, VOL⁵ entries were obtained in acetonitrile and VOL³, VOL⁶ were obtained in the mixed solvent of acetonitrile and DMF in the 3:2 ratio in 24 h period. Catalytic reaction with VOL³ is carried out in heterogeneous media.

^b Electrochemical measurement made in anhydrous acetonitrile or DMF containing 0.1 tetrabutyl ammonium hexafluorophosphate (TBAH) vs. AgCl/Ag. Irreversible reduction was observed for the complexes at potential less than –1500 mV accompanied by decomposition of complexes.

^c Repartition of different products identified (represent almost 90% of all the products).

oxidized to a mixture of cyclooctene epoxide, cyclooctene 1-ol and cyclooctene 1-one as major products.

The oxygenated products was monitored by quantitative GC determination. Samples were quenched by the addition of excess triphenyl phosphine to destroy the remaining peroxide. The products were distinguished by GC–MS coupling and also Epoxide were identified by comparison with authentic samples. The results of the cyclooctene oxidation distributions are shown in Fig. 3 and Table 1. Only relative ratios of three major products are represented in Fig. 3 as repartition of the different products identified.

At the end of the reaction time, vanadium complexes precipitate by the evaporation of solvent under vacuum. There is not any evidence that shows vanadyl complexes changed or degraded because the vanadyl complexes have same UV–vis spectra and cyclic voltammograms before and after of catalytic reaction. Therefore, during 24 h these compounds play as robust catalyst without any degradation. The results show good catalytic performance (average turnover frequency up to 380 h⁻¹) and moderate selectivity (up to 58% epoxide) comparing to those reported in our previous works for cyclohexene oxidation [7,8].

Several control experiments were performed. The presence or absence of light does not affect on catalysts. The salen catalysts are very stable to oxidative degradation under reaction conditions. In the absence of catalyst, or just in the presence of ligand, little or no oxidation occurs. However, after recovering, washing with acetone and drying of the catalyst, epoxidation

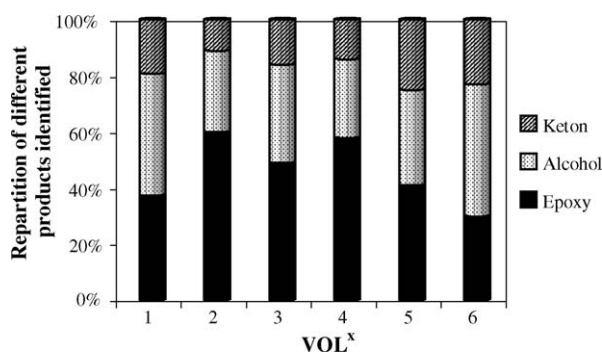


Fig. 3. Repartition of different products identified for the aerobic oxidation of cyclooctene catalyzed by VOL^x, x=1–6.

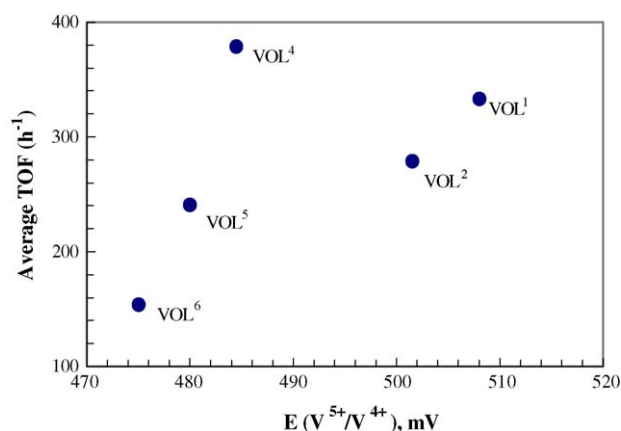


Fig. 4. Plot of average turnover frequency (h⁻¹) for catalytic cyclooctene oxidation vs. E_{redox}^0 (V⁵⁺/V⁴⁺)/mV for VOL^x, x=1–6 (except x=3) complexes.

of cyclooctene under identical condition occurred with similar yields and selectivity. VOL⁴ is the most active complex, achieving approximately 9120 turnovers in a 24 h period. Its performance is shown as a function of redox potential in Fig. 4.

4. Conclusion

Development of new catalysts has been done towards for the synthesis of epoxides in a more environmental friendly way. We have found that the mono oxovanadium(IV) complexes of the N₂O₂ donor set ligands are able to catalyze selective epoxidation of cyclooctene with high yield, using O₂ in polar solvents. In the presence of dioxygen, vanadyl catalyst and acetonitrile or DMF as solvent, cyclooctene is oxidized to mixture of cyclooctene oxides. Systematic ancillary ligand substitutions have allowed V⁵⁺/V⁴⁺ reduction potentials to be tuned over a range of approximately 33 mV. Reactivity of the catalysts would be modulated by control of ligand substitution. Almost all vanadyl complexes have good activities for cyclooctene epoxidation by dioxygen under mild conditions, using inexpensive and readily available ligands. Because of similarity of electronic structure of cyclohexene and cyclooctene, the results are comparable with those we reported for cyclohexene oxidation [6–8]. Basically there is no significant different. A little different between them is due to

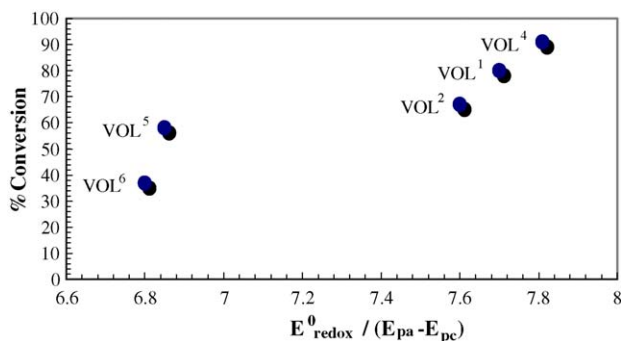


Fig. 5. Plot of activity for catalytic cyclooctene oxidation vs. $[E^0_{redox}/\Delta E_p]$ for VOL^x , $x=1-6$ (except $x=3$) complexes.

more cyclic distortion of cyclooctene rather than cyclohexene. This steric effect causes lower yield if the reaction goes through inner-sphere mechanism. Upon oxidation, the green compounds turned to an intense violet or blue color.

Re-reduction yielded VOL^x unchanged. The process could be repeated many times without any evidence of chemical degradation. The fact that the reduction is completely reversible indicates that the five-coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale. From these results, we concluded that the redox process of all vanadyl Schiff base complexes used in this study is one-electron transfer reaction.

Because of low oxidation selectivity of the VOL^x catalysts and according to Gray [15] mechanism for selectivity of olefin epoxidation by metal complexes, initial auto-oxidation of cyclooctene generates allylic hydroperoxides. Then the vanadyl complexes can decompose to intermediate organic peroxides via a heterolytic mechanism rather than a homolytic one. Increasing of epoxide product by adding small amount of an electrolyte to the reaction cell is our evidence for this path. In this step of study, the observation is not enough to establish an electron transfer or oxygen transfer process, therefore assignment of a precise catalytic cycle is too difficult. However it seems mechanism is not proceed by a cation radical path. We proposed oxidation of the cyclooctene by cyclooctenyl hydroperoxide afford through an inner-sphere six coordinate oxovanadium species that is probably the active oxidizing species [16].

The correlation between potential and activity seems to be subject to subtle structural effects. The results show that catalytic activity increases with decreases in the number of electron-donating groups. The vanadyl complexes with strongly donor ligands, are more stable during the oxidation process.

Comparing GC and Redox potential results, shows a correlation between selectivity and activity. In general, conversion percent decreases by increasing of ΔE_p and decreasing of E^0_{redox} . Maximum percent of conversion and activity is seen in case of VOL^1 and VOL^4 which have minimum ΔE_p and maximum E^0_{redox} .

We found, the catalyst activity has a direct correlation with $E^0_{redox}/\Delta E_p$ ratio as shown in Fig. 5. The conversion percentages increase with increasing $E^0_{redox}/\Delta E_p$ ratio of V^{5+}/V^{4+} couples. In fact, this subtlety may offer additional possibilities for manipulating reactivity, because both electronic and steric factors can be controlled independently. Ligand bulkiness caused by substitution may strongly influence the overall activation energy, relative to the less distributed salen system. Such situation provides an opportunity for connecting the results of basic research to developed practical catalysts. The catalytic system described here is an efficient method for the epoxidation of cyclooctene, with the advantages of high activity, selectivity and short reaction times.

Our works are progress towards the development of an efficient heterogeneous catalyst for epoxidation of olefins and towards the improvement of reaction selectivity.

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