Application in the cyclohexane oxidation of a scorpionate oxovanadium(IV) complex: synthesis, structure, and properties of $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$

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Application in the cyclohexane oxidation of a scorpionate oxovanadium(IV) complex: synthesis, structure, and properties of VO(C$_5$H$_7$O$_2$)(BC$_9$H$_7$N$_6$I$_3$)

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An oxovanadium(IV) complex, VO(C$_5$H$_7$O$_2$)(BC$_9$H$_7$N$_6$I$_3$), derived from hydrotris(4-iodinpyrazolyl) borate was designed and synthesized at room temperature in methanol. The complex was characterized by elemental analysis, IR spectra, UV-Vis spectroscopy, and single-crystal X-ray diffraction. The structural analysis shows that the vanadium(IV) center possesses a distorted-octahedral geometry with a N$_3$O$_3$ core, containing a tridentate hydrotris(4-iodinpyrazolyl) borate with nitrogen as three donors. The complex is the first structurally characterized example of a vanadium(IV) complex with hydrotris(4-iodinpyrazolyl)borate. It was used as a catalyst for cyclohexane oxidation under mild conditions and the effects of a variety of factors such as amount of acid and H$_2$O$_2$, the kind of solvent, as well as temperatures were evaluated; the maximum turnover number value reaches 321.

Keywords: Oxovanadium complexes; Hydrotris(4-iodinpyrazolyl)borate; Crystal structure; Quantum chemistry calculations; Cyclohexane oxidation

1. Introduction

Vanadium compounds have rich applications [1–3] in a variety of biochemical processes: haloperoxidation [4], phosphorylation [5], nitrogen fixation [6], and insulin mimicking [7], as well as chemical processes including: (i) the oxidation or epoxidation of hydrocarbons (e.g., cyclopentane [8], cyclohexene [8–10], cyclooctane [11, 12], cyclooctene [11], methyl cyclohexane, methylbenzene, ethylbenzene [12], styrene derivatives [13], norbornene [14], 3,5-di-tert-butylcatechol [5], alcohol [15], isopropanol [16], benzene [17], and other aromatic [12]), (ii) the bromination of 1,3,5-trimethoxybenzene [18] and 2,6-dimethylphenol [15], and (iii) the polymerization of ethylene and ring-opening polymerization of caprolactone [19–23]. In particular, oxidation of saturated hydrocarbons provides promising methods toward the use of unreactive compounds as raw materials for organic syntheses. A good example is the oxidation of cyclohexane,

with the main products as cyclohexanol and cyclohexanone, which are important raw materials for the production of adipic acid and caprolactam used in the manufacture of nylon-6, 6 and nylon-6, respectively [24]. Efforts have been devoted to achieve more active systems under milder condition. Pombeiro and Mishra *et al.* reported that the overall conversion of cyclohexane with dioxygen or hydrogen peroxide by using bis(maltolato)oxovanadium complexes [25], Schiff-base V complex [26], V-scorpionate complexes [10], and half-sandwich scorpionate vanadium [9] as catalysts is 15%, 13%, 13%, and 25%, respectively. Fernnde *et al.* found that the turnover number (TON, moles products/mol catalyst) in cyclohexane oxidation promoted by a dioxovanadium(V) complex was 308 (e.g., conversion of 69%) [17]. The overall conversion of cyclohexane was 47% when an oxovanadium complex with an imidazole-rich tripodal ligand was used as a catalyst and H_2O_2 as oxidant [11].

Besides attractive catalytic properties, vanadium in either a cationic or anionic form can complex with many acceptors. When the metal is coordinated with ligands, more soluble and less toxic compounds can be achieved [27–29]. Consequently, studies on syntheses and properties of new vanadium complexes with diverse ligands are important. The scorpionate ligand, hydrotris(pyrazol-1-yl)borate (Tp^-), has a strong tendency to form full-sandwich complexes, while the hydrogen atoms at the 3,4,5 positions of the pyrazole ring may be substituted by other groups. If one begins with an appropriate pyrazole, the corresponding substituted ligand may be synthesized. Oxovanadium complexes with hydrotris(pyrazol-1-yl)borate (Tp) have appeared [30–38]. Our group has a long-standing interest in investigation of oxovanadium complexes with poly(pyrazolyl)borate ligands. We have reported a series of oxovanadium complexes, such as $TpVO(H_2B(pz)_2)$ [39], $TpVO(pzH)$ $(2,4\text{-Cl-}C_6H_3\text{-}OCH_2COO)$, $TpVO(pzH)(C_6H_5\text{-}OCH_2COO)$, $TpVO(pzH)(p\text{-Cl-}C_6H_4\text{-}COO)$, $TpVO(pzH)(3,5\text{-}NO_2\text{-}C_6H_3\text{-}COO)$ [40], $TpVO(O_2)(pzH)$ [41], and $TpVO(acac)$ [42]. However, stable mononuclear oxovanadium(IV) complexes with hydrotris(4-iodinpyrazolyl)borate ligand, which are analogous to Tp, have not been reported.

Here, we report the first structural example of an oxovanadium(IV) complex with hydrotris(4-iodinpyrazolyl)borate: $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ (scheme 1). The catalytic properties of the complex have also been studied in the hydrogen peroxide promoted oxidation of cyclohexane under mild conditions.
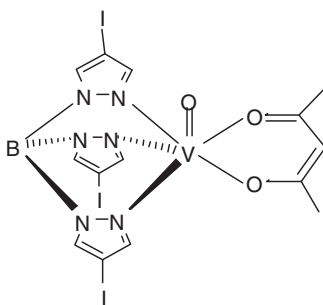
Scheme 1.   The diagram of $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$.

2. Experimental

2.1. *Chemical materials*

All chemicals used were of analytical grade and without purification. Hydrotris(4-iodinpyrazolyl)borate was synthesized according to the literature procedure [43, 44]. The syntheses were carried out at room temperature. A 30% aqueous solution of hydrogen peroxide was used as primary oxidant in oxidation reactions.

2.2. *Physical measurements*

Elemental analyses (C, H, and N) were performed on P.E. 240C automatic analyzer. Infrared (IR) spectra were determined with a JASCO FT/IR-480 PLUS Fourier Transform spectrometer (200–4000 cm^{-1}, with pressed KBr pellets). UV-Vis spectra were determined by a JASCO V-570 UV-Vis spectrometer (200–1100 nm, as solids). The products of the oxidation were analyzed by a Shimadzu GC-16A series gas chromatograph equipped with a flame ionization detector (FID) and a capillary column (PG2000, column length: 30 m; internal diameter: 0.25 mm).

2.3. *Preparation of $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$*

A methanolic solution of hydrotris(4-iodinpyrazolyl)borate potassium (0.28 g, 0.5 mmol) was added dropwise to a methanolic solution (10 mL) of vanadyl acetylacetonate VO(acac)$_2$ (0.13 g, 0.5 mmol) with continuous stirring for *ca* 3 h to get a violet mixture. The filtrate from the mixture was placed at room temperature for slow evaporation. Two days later, blue crystals suitable for X-ray were obtained and dried under vacuum. Yield (based on V): 0.29 g, 78.67%. Anal. Calcd for C$_{14}$H$_{14}$N$_6$O$_3$BI$_3$V (%): C, 22.22; H, 1.86; N, 11.11. Found (%): C, 22.18; H, 1.91; N, 11.03. IR (KBr, v, cm^{-1}): 3448, 3102, 2521, 1703, 1582, 1517, 1370, 1318, 1281, 1225, 1168, 1118, 1024, 946, 854, 828, 796, 716, 611, 467, 358. UV-Vis (λ_{max}, nm): 256, 362, 532, 776.

2.4. *X-ray data collection and refinement of crystal structure*

The crystal of the complex was mounted on a glass fiber for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and a ω scan mode. All measured independent reflections ($I > 2\sigma(I)$) were used in the structural analyses and semi-empirical absorption corrections were applied using SADABS [45].

The structure was solved using direct methods with SHELXS-86 and refined using SHELXL-97 [46]. All hydrogen atoms were positioned geometrically and refined using a riding model. The non-hydrogen atoms were refined with anisotropic thermal parameters. The crystallographic data and experimental details of the data collection, as well as the structure refinement are given in table 1. Diagrams were made with Diamond and all calculations were performed on a Pentium 4 computer.

Table 1. X-ray structural details for $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$.

Empirical formula	$C_{28}H_{28}N_{12}O_6B_2I_6V_2$
Formula weight	1513.52
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions (Å, °)	
a	12.658(6)
b	13.607(7)
c	15.023(7)
α	97.793(8)
β	106.280(7)
γ	98.758(7)
Volume (Å^3), *Z*	2411(2), 2
Calculated density (Mg m^{-3})	2.085
$F(000)$	1404
Crystal size (mm^3)	$0.64 \times 0.07 \times 0.04$
μ (Mo-Kα) (cm^{-1})	42.77
Reflections collected	10,212
Independent reflections [$I > 2\sigma(I)$]	6643
Parameters	513
$\Delta(\rho)$ (e Å^{-3})	2.129–1.900
Goodness-of-fit on F^2	1.041
R[a]	0.0569(0.0938)[b]
wR_2[a]	0.1214(0.1417)[b]

[a]$R = \Sigma||F_o| - |F_c||/|\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)^{1/2}]$; [$F_o > 4\sigma(F_o)$].
[b]Based on all data.

2.5. *Experimental for catalytic oxidation*

Oxidation reactions were carried out in air (atmospheric pressure) in Schlenk tubes. In a typical experiment, 0.0004 g of $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ was dissolved in 3.00 mL of solvent. Then H_2O_2 and HNO_3 were added followed by 0.34 g of cyclohexane. The mixture was stirred at the selected temperature for selected times.

For product analyses, 0.05 g of methylbenzene (internal standard) and 3.00 mL of diethyl ether (to extract substrate and organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (0.8 μL) was taken from the organic phase and analyzed by a gas chromatography (GC) equipped with a capillary column and an FID by the internal standard method. Blank experiments confirmed that no cyclohexanol or cyclohexanone were formed in the absence of the metal catalyst under the same conditions.

3. Results and discussion

3.1. *Synthesis*

At room temperature, $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ can be easily synthesized by the reaction of $VO(acac)_2$ with hydrotris(4-iodinpyrazolyl)borate potassium in CH_3OH (scheme 2). Crystals of the complex suitable for X-ray diffraction were readily grown in MeOH. If the starting $VO(acac)_2$ was replaced by $VOSO_4 \cdot 3H_2O$, however, the targeted complex is not obtained. The resulting complex is quite stable in the solid state at room
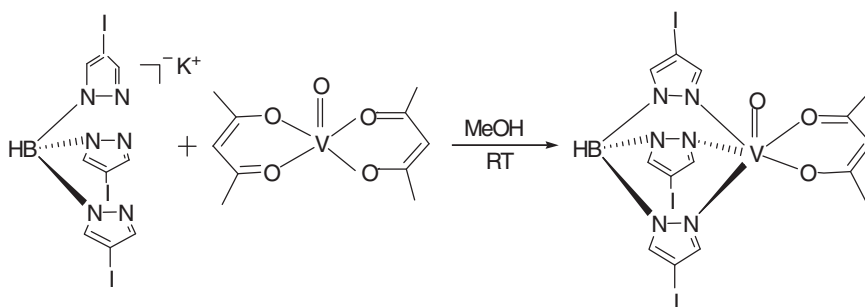
Scheme 2.   General procedure for the preparation of $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$.
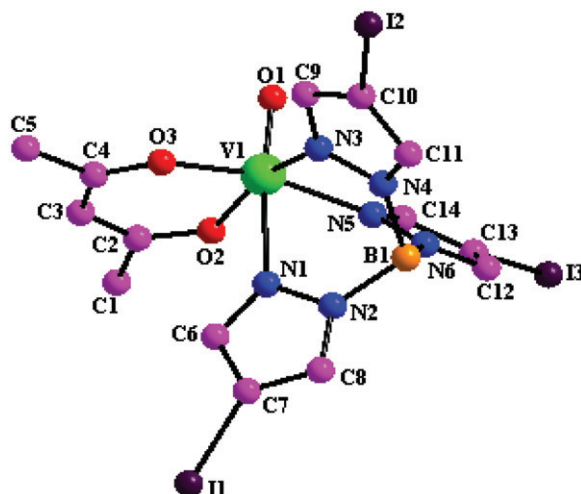
Figure 1.   The molecular structure of $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ (all hydrogen atoms are omitted for clarity).

temperature and also soluble in CH_2Cl_2, CH_3CN, and THF. On the other hand, it is insoluble in hexane and ether.

3.2. *Structural description of the complex*

The structure of the complex with the atom-numbering scheme is depicted in figure 1. The principal bond lengths and angles for the compounds are listed in table 2. There are two independent $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ molecules in the asymmetric unit. Since little differences among the corresponding bond lengths and angles of the two molecules can be observed, we analyze only one molecule, with the structure shown in figure 1. V1 is six-coordinate to O1 (a terminal oxygen), N1, N3, N5 from the hydrotris (4-iodinpyrazolyl)borate ligand and O2 and O3 from acetylacetone, forming a distorted octahedral geometry. The deviations of O2, O3, N3, and N5 of the least-squares plane are −0.0277(42), 0.0280(42), −0.0267(40), and 0.0264(40) Å, respectively, revealing that

Table 2. Selected bond distances and angles for $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$.

1a

V1–O1	1.579(8)	V1–O2	1.984(8)	V1–O3	1.976(8)
V1–N1	2.313(8)	V1–N3	2.113(1)	V1–N5	2.118(9)
O1–V1–O3	99.9(4)	O1–V1–O2	102.6(4)	O3–V1–O2	89.3(3)
O1–V1–N3	96.3(4)	O3–V1–N3	88.7(3)	O2–V1–N3	161.1(3)
O1–V1–N5	95.8(4)	O3–V1–N5	164.1(3)	O2–V1–N5	89.5(4)
N3–V1–N5	87.3(4)	O1–V1–N1	172.4(4)	O3–V1–N1	85.0(3)
O2–V1–N1	83.2(3)	N3–V1–N1	77.9(3)	N5–V1–N1	79.2(3)

1b

V2–O4	1.580(8)	V2–O5	1.990(8)	V2–O6	1.992(8)
V2–N7	2.114(1)	V2–N9	2.093(9)	V2–N11	2.314(9)
O4–V2–O5	102.6(4)	O4–V2–O6	99.8(4)	O5–V2–O6	88.3(3)
O4–V2–N9	95.7(4)	O5–V2–N9	161.6(4)	O6–V2–N9	90.7(4)
O4–V2–N7	94.0(4)	O5–V2–N7	88.9(4)	O6–V2–N7	166.2(4)
N9–V2–N7	87.8(4)	O4–V2–N11	170.8(4)	O5–V2–N11	83.7(3)
O6–V2–N11	87.0(3)	N9–V2–N11	77.9(3)	N7–V2–N11	79.3(3)

the atoms are an approximate plane. V1, O1, and N1 from the axial position lay 0.3086(45), 1.8854(86), and −1.9975(91) Å out of the equatorial plane, indicating that V1 is toward the oxo oxygen O1 *trans* to N1. There are differences among the coordination ability of the three nitrogen atoms of hydrotris(4-iodinpyrazolyl)borate. The V–N distance *trans* to V = O is longer than the V–N bonds in the equatorial plane, a consequence of the strong *trans* influence of the terminal *oxo* group. The angle of O1–V1–N2 is 172.4(4)°.

Comparing the bond lengths and angles to similar oxovanadium complexes, it is found that: (i) V–O distances from acac are in the range of 1.976(8)–1.992(8) Å, slightly shorter than the corresponding bond distances in TpVO(acac) and Tp*VO(acac)·CH_3CN (1.984(8)–1.996(8) Å) [42] while the average O–V–O angle from acac (88.8(3)°) is similar to the corresponding angle in TpVO(acac) (88.9(7)°) and larger than that of Tp*VO(acac)·CH_3CN (86.6(2)°), (ii) the V = O bond lengths (1.579(8) and 1.580(8) Å) are slightly shorter than the corresponding bond distances in TpVO(acac) (1.590(2) Å) and Tp*VO(acac)·CH_3CN (1.592(5) Å), but the lengths of V–N bond *trans* to the V = O (2.313(8) and 2.114(1) Å) are slightly shorter than that of the bond distances in TpVO(acac) (2.338(2) Å) and Tp*VO(acac)·CH_3CN (2.368(7) Å), while the O–V–N_{trans} angles in the complex (172.4(4)° and 161.6(4)°) are slightly narrower than the corresponding angles in TpVO(acac) (173.5(7)°) and Tp*VO(acac)·CH_3CN (175.4(2)°). This may be related to electronic effects, as well as steric hindrance of the ligands.

Intermolecular hydrogen bonds also exist among the terminal oxygen atoms and C–H groups of the hydrotris(4-iodinpyrazolyl)borate as shown in figure 2. A ribbon chain is formed with the dimeric molecules by interactions of C6–H6A···O4[a] (2.463(5) Å, 134.2(4)°, [a]=1 − x, 1 − y, 1 − z) and C28−H28A···O1[b] (2.518(2) Å, 141.8(4)°, [b]=1 − x, −y, 1 − z) along the *b*-axis.

3.3. *IR spectra*

In the IR spectrum of the complex as shown in "Supplementary material," bands at 3102 and 3117 cm^{-1} are assigned to C–H from pyrazole. The characteristic band
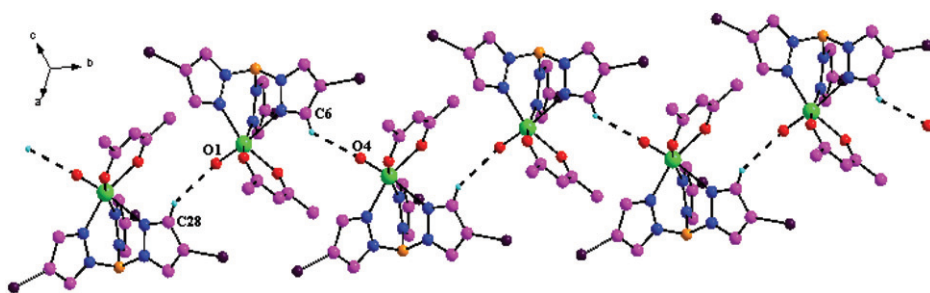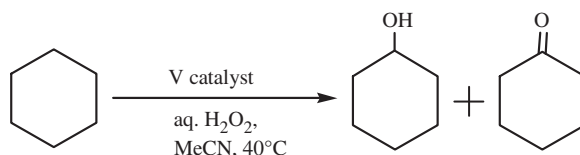
Figure 2. 1-D network of hydrogen-bonding found in $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ along the *b*-axis (all hydrogen atoms except the hydrogen bonds are omitted for clarity).

Scheme 3. Diagram of cyclohexane oxidation process promoted by $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$.

at $2521\,cm^{-1}$ corresponds to B–H stretch of the hydrotris(4-iodinpyrazolyl)borate ligands [47]. A strong and sharp vibration of $V=O$ appears at $946\,cm^{-1}$, and the asymmetric and symmetric stretching vibrations of acetylacetone are at 1582, $1517\,cm^{-1}$ and 1370, $1318\,cm^{-1}$, respectively. Besides these general features, other groups of the complex are also present; bands at 467, $457\,cm^{-1}$ correspond to the V–O stretch and 358, $374\,cm^{-1}$ are attributed to the V–N stretches [48].

3.4. *UV-Vis spectra*

The UV-Vis absorption spectrum of the complex is recorded as a solid sample (shown in Supplementary material). The sharp and strong high-energy absorption at 258 nm is assigned to π–π^* transition of the aromatic-like chromophore from hydrotris (4-iodinpyrazolyl)borate. The band at 362 nm is attributed to the charge transitions of the hydrotris(4-iodinpyrazolyl)borate to the metal LMCT. The broad bands at 532 and 776 nm are assigned to d–d transitions of vanadium [39, 42].

3.5. *Catalytic activity studies*

The complex was used to study the catalysis of the oxidation of cyclohexane in acetonitrile and acidic medium, with H_2O_2 as primary oxidant and according to the overall reaction (scheme 3). Thus, the effect of oxidant concentration (moles of H_2O_2 per moles of catalyst), acid concentration (moles of HNO_3 per moles of catalyst), nature of solvent, and temperature of the reaction were studied.

As a "green" oxidant whose by-products are water and dioxygen, hydrogen peroxide is used as the main oxidizing agent in the system. The effect of oxidant concentration on
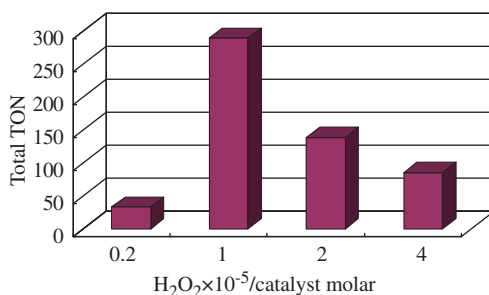
Figure 3. Effect of H_2O_2 concentration on cyclohexane oxidation with $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$. Reaction conditions: cyclohexane (0.34 g), H_2O_2 ($H_2O_2 \times 10^{-5}$/catalyst molar ratio = 0.2, 1, 2, and 4), HNO_3 (0.02 g), catalyst (0.0004 g), acetonitrile (3 mL), 3 h, 40°C.
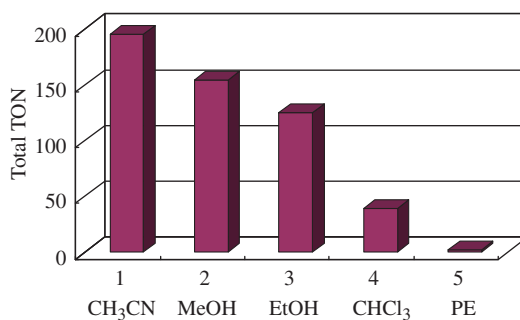

Figure 4. Effect of solvent on cyclohexane oxidation with $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$. Reaction conditions: cyclohexane (0.34 g), HNO_3 (0.02 g), H_2O_2 (0.90 g), catalyst (0.0004 g), solvent (3 mL), 4 h, 40°C.

the oxidation of cyclohexane catalyzed by the complex is illustrated in figure 3. Different $H_2O_2 \times 10^{-5}$/catalyst molar ratios (0.2 : 1, 1 : 1, 2 : 1, and 4 : 1) were studied, when keeping the fixed amount of cyclohexane (0.34 g), HNO_3 (0.02 g), and catalyst (0.0004 g) in 3 mL of acetonitrile at 40°C for 3 h. The complex displayed the lowest catalytic activities (overall TON of 34) when the $H_2O_2 \times 10^{-5}$/catalyst molar ratio was only 0.2 : 1. The observation suggested that the amount of H_2O_2 was not enough for cyclohexane oxidation. When the ratio increased to 1 : 1 (0.90 g of H_2O_2), the highest TON of 289 was achieved. With further increase in the ratio to 2 : 1 and 4 : 1, the catalytic activities decreased unexpectedly, with TON of 138 and 85, respectively. This may be caused by further oxidation to the by-product cyclohexylhydroperoxide [17], which led to the decrease of product (i.e., cyclohexanol and cyclohexanone) conversion. Excess oxidants are, thus, not suitable for the formation of targeted products.

A total of five different solvents CH_3CN, MeOH, EtOH, $CHCl_3$, and petroleum ether (PE) (3 mL) were evaluated for catalysis, while keeping fixed the amount of cyclohexane (0.34 g), HNO_3 (0.02 g), H_2O_2 (0.90 g), and catalyst (0.0004 g) at 40°C and running for 4 h. Figure 4 illustrates the influence of solvent on the catalytic oxidation of cyclohexane by $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$. The highest TON of 196 was obtained in acetonitrile. The catalytic activity of the complex decreases in order of relative dielectric constants [49], acetonitrile ($\varepsilon/\varepsilon_0 = 37.5$) > methanol (32.7) > ethanol (26.6) > chloroform
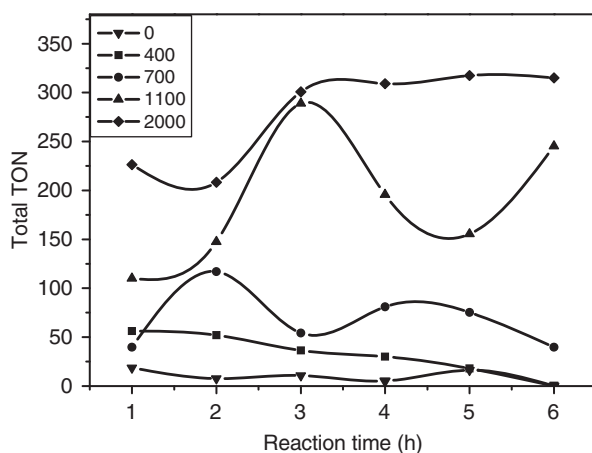
Figure 5. Effect of HNO$_3$ concentration on cyclohexane oxidation with VO(C$_5$H$_7$O$_2$)(BC$_9$H$_7$N$_6$I$_3$). Reaction conditions: cyclohexane (0.34 g), H$_2$O$_2$ (0.90 g), HNO$_3$ (HNO$_3$/catalyst molar ratio = 0, 400, 700, 1100, and 2000), catalyst (0.0004 g), CH$_3$CN (3 mL), 40°C.

(4.9) > PE (∼2) (e.g., there is a good correlation between the solvent polarity ($\varepsilon/\varepsilon_0$) and the TON of cyclohexane oxidation), which is in good accordance with that reported in the literature [12]. The highest TON in acetonitrile is possibly caused by the highest dielectric constant of acetonitrile; however, it has been reported [50] that acetonitrile, upon reaction with H$_2$O$_2$, forms the peroxycarboximidic acid MeC(=NH)OOH which is a good oxygen transfer agent. Since acetonitrile is the typical solvent used in this type of reactions due to its high resistance to oxidizing agents and good solubility for alkane and organic products, the amount of CH$_3$CN in the reaction mixture was studied (not shown). The formation of products is not observed in the absence of acetonitrile; increase in the volume of CH$_3$CN promotes the catalytic activity, reaching a suitable TON with 3 mL of acetonitrile. Above this volume, the reaction comes to almost steady state and only minor increase of TON is observed to 10 mL. To evaluate the catalysis during catalytic oxidations, we used 3 mL acetonitrile as reaction solvent.

Five different molar ratios of HNO$_3$/catalyst (i.e., 0, 400, 700, 1100, and 2000) were considered to evaluate the effect of nitric acid concentration on the oxidation of cyclohexane catalyzed by the complex while keeping fixed the amount of cyclohexane (0.34 g), H$_2$O$_2$ (0.90 g), catalyst (0.0004 g), and CH$_3$CN (3 mL) at 40°C and running for 6 h. The progress of the reaction was regularly monitored at different time intervals using GC analysis. As shown in figure 5, the addition of HNO$_3$ results in enhancement of activity (e.g., the overall TON increases from 0 to 315 on changing the acid-to-catalyst molar ratio from 0 to 2000). TON of 11 was obtained in the absence of nitric acid. When the ratio of HNO$_3$/catalyst equals 400, the overall TON decreased straightly from 52 to 0 with reaction time from 1 to 6 h and was almost the same as that in the condition without HNO$_3$ either at the 5th or the 6th hour, which indicates that the amount of nitric acid was not enough for the reaction with the ratio of 400 : 1 and consumed completely at about 5 h. Over this ratio, the overall TON increased and the maximum (315) was achieved when the ratio of HNO$_3$/catalyst molar was 2000 : 1 at 6 h, although it was not much larger than that of 1000 : 1 (0.02 g of HNO$_3$) at 3 h (TON of 289).
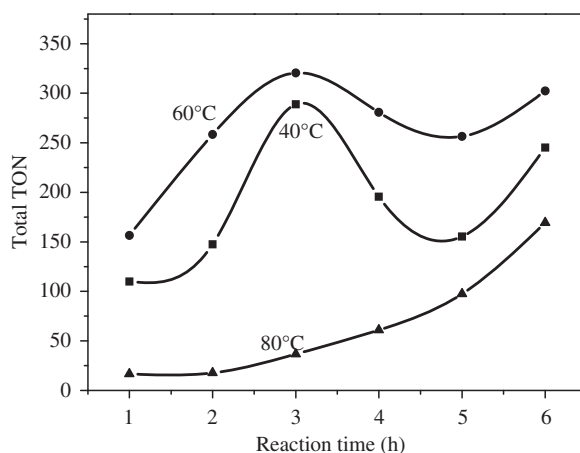
Figure 6. Effect of temperature on cyclohexane oxidation with $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$. Reaction conditions: cyclohexane (0.34 g), H_2O_2 (0.90 g), HNO_3 (0.02 g), catalyst (0.0004 g), CH_3CN (3 mL), at 40°C, 60°C, or 80°C.

Figure 7. Effect of temperature on cyclohexane conversion with $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$. Reaction conditions: cyclohexane (0.34 g), H_2O_2 (0.90 g), HNO_3 (0.02 g), catalyst (0.0004 g), CH_3CN (3 mL), at 40°C, 60°C, or 80°C.
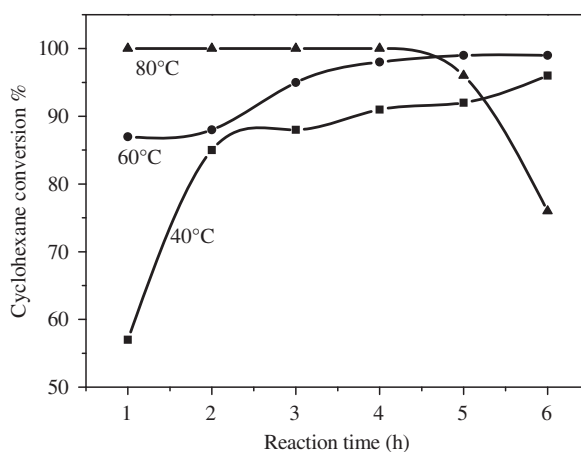
Finally, 20°C, 40°C, 60°C, and 80°C were chosen to evaluate the effect of temperature on oxidation of cyclohexane catalyzed by $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ while keeping fixed the amount of cyclohexane (0.34 g), H_2O_2 (0.90 g), HNO_3 (0.02 g), catalyst (0.0004 g), and CH_3CN (3 mL) running for 6 h. No cyclohexanol or cyclohexanone could be detected when the oxidation was carried out at 20°C (not shown). As can be seen in figure 6, when the temperature increased to 40°C or 60°C, the complex displays good catalytic activities with maximum TON of 289 and 321, respectively, upon 3 h reaction time. But when the temperature was increased to 80°C, the overall TON decreased. To determine a reason, the cyclohexane conversion with reaction time at different temperatures was studied (figure 7). Cyclohexane conversion increased from 85% to 96% and 88% to 99% at 40°C

and 60°C, respectively. When the temperature increased to 80°C, the cyclohexane conversion remains 100% from the beginning to about 4.5 h and then decreases. The observation may be attributed to the formation of cyclohexylhydroperoxide, which may be the main oxidation product at such high temperature (80°C), resulting in the low total TON of cyclohexanol and cyclohexanone (figure 6) and high conversion of cyclohexane (figure 7) before 4.5 h. However, the cyclohexylhydroperoxide has a tendency to decompose to CO_2, H_2O, and cyclohexane. So when the reaction time was greater than 4.5 h, some cyclohexylhydroperoxide decomposed back to cyclohexane, which leads to a decrease of cyclohexane conversion. To avoid competitive oxidation, and save energy, 40°C is determined to be better for the oxidation of cyclohexane to cyclohexanol and cyclohexanone with the complex as a catalyst.

4. Conclusion

An oxovanadium(IV) complex, $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$ (**1**), was synthesized by the reaction of $VO(acac)_2$ with hydrotris(4-iodinpyrazolyl)borate potassium in MeOH, the first structurally characterized example of a vanadium(IV) complex with hydrotris(4-iodinpyrazolyl)borate. The catalytic ability of the vanadium complex was evaluated using H_2O_2 as oxidant for cyclohexane oxidation. Parameters such as solvent, temperature, acid, and oxidant concentration were studied to optimize both activity and selectivity of the oxidative process. Under optimized conditions (0.30 g of cyclohexane, 0.90 g of H_2O_2, 0.02 g of HNO_3, and 0.0004 g of catalyst in 3 mL CH_3CN for 3 h at 40°C), cyclohexanol and/or cyclohexanone were obtained with good to excellent conversion (TON of 321) as main products of the hydrocarbon oxidation, which is superior to those reported in the literature. Further studies will be devoted to gain details on the mechanism within the family of catalysts or similar derivatives, and to extend applicability toward catalytic synthetic oxidations.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge by quoting the publication citation and deposition number CCDC for $VO(C_5H_7O_2)(BC_9H_7N_6I_3)$: 748101, from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary material associated with the article can be found free of charge in the online version.

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