

The effect of oxalic acid and glyoxal on the VO(acac)₂-catalyzed cyclohexane oxidation with H₂O₂

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ABSTRACT

A new protocol for the effective oxidation of cyclohexane in acetonitrile at 40 °C and atmospheric pressure into cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide using hydrogen peroxide as the oxidant, vanadyl(IV)-acetylacetonate as the catalyst, oxalic acid and glyoxal as additives is presented with some reaction mechanism proposals.

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1. Introduction

Despite the extensive efforts which have been undertaken to carry out the selective oxidation of C–H bonds of inactivated hydrocarbons, the research for effective and energy-spared catalytic systems remains the subject of intensive investigations [1]. Of particular interest is the application of such protocol to the cyclohexane oxidation due to extended appliance of its oxidized products, i.e. cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide. Indeed, these products are used to manufacture as much as 2.3×10^6 T adipic acid and 4.4×10^6 T of ϵ -caprolactam per year [2,3]. The contemporary industrial two-stage cyclohexane oxidation process is achieved at 160–170 °C and 1.2–1.5 MPa of air. In about 30 min, such severe conditions led to 4–6% conversion of C₆H₁₂ into the mixture of C₆H₁₁OH and C₆H₁₀O with 75–80% selectivity [4]. Such characteristics do not satisfy the economical constrains any more [3]. Promising results have been reported using homogeneous [5,6], heterogeneous [7] or bio-inspired [8–11]

catalytic systems, but, for the most of them, cyclohexane conversion does not exceed 20–30% [12,13]. Chemical yields up to 30% [10] or 39% [11] have been obtained but with turnover numbers (*ton*) lower than 380. The conversion can be improved to 90% but with a diluted heterogeneous vanadium phosphorous oxide mixture which is not recyclable; at 65 °C for 20 h, this leads to a moderate *ton* (300–400) [14], which is actually much lower to the industrial ones (1000–10,000) reached more than 50 years ago [15].

Previously, we have disclosed that the rate, yield and *ton* of the cyclohexane oxidation with H₂O₂ catalyzed by VO(acac)₂ (**1**) are enhanced in the presence of glyoxal (H(O)CC(O)H, **2**) [16]. Now, we report that the VO(acac)₂-catalyzed process is strongly improved using both glyoxal and oxalic acid (HO(O)CC(O)OH, **3**) as additives. Oxalic acid has been chosen because it can be derived from **2** under the oxidation conditions.

2. Experimental

2.1. Chemicals

The commercial aqueous solutions of glyoxal (40 wt.%) and hydrogen peroxide (35 wt.%) in water (both from Fluka) have been concentrated by a vacuum distillation at 45 °C/10 mm Hg to 80 and 70 wt.%, respectively (Caution: risk of explosion in the case

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Table 1Oxidation of cyclohexane in MeCN, 1.8 mol L⁻¹ H₂O₂, 40 °C, 5 h.

Entry	C ₆ H ₁₂ , mol L ⁻¹	1, × 10 ⁴ , mol L ⁻¹	2 3		Conv., %	Selectivity, %			ton, mol mol ⁻¹ (1)	tof ^a , mol mol ⁻¹ (1) h ⁻¹	ΔH ₂ O ₂ ^b , %
			mol L ⁻¹			C ₆ H ₁₁ OH	C ₆ H ₁₀ O	C ₆ H ₁₁ OOH			
1	1.8	5.0	–	–	1.6	33	62	5	33	19	48
2	1.8	5.0	0.18	–	3.8	30	44	26	72	35	75
3	1.8	5.0	–	0.001	1.7	1	8	91	51	37	52
4	1.8	5.0	0.18	0.001	3.4	14	8	72	109	66	97
5	1.8	5.0	–	0.14	5.2	47	10	43	173	72	80
6	1.8	5.0	–	0.045	7.6	43	13	44	253	123	90
7	1.8	1.0	–	–	0.7	38	46	16	145	36	21
8	1.8	1.0	0.18	–	1.2	26	52	22	228	61	29
9	1.8	1.0	0.18	0.014	4.0	2	23	75	660	234	84
10	1.8	0.5	0.18	0.014	7.2	3	21	76	2416	798	70
11	1.8	0.5	0.18	0.004	3.6	4	38	58	1216	702	60
12	1.8	0.5	0.18	0.002	3.6	4	19	77	1167	600	40
13	0.36	0.5	0.18	0.014	23	29	51	20	1472	481	55
14	0.18	0.5	–	0.014	30	22	44	34	944	246	34
15	0.18	0.5	0.18	0.014	31	32	55	13	992	522	43
16	0.18	0.5	0.18	0.045	28	41	50	9	896	401	44
17 ^c	1.8	0.5	–	0.03	0.2	29	29	42	56	24	3
18 ^d	1.8	0.5	0.18	–	0.3	20	40	40	80	18	7
19 ^d	1.8	0.5	0.18	0.014	4.1	6	33	61	1310	463	53
20 ^e	1.8	0.5	0.18	0.014	3.1	2	48	50	992	186	28
21 ^f	1.8	0.5	–	–	0.6	16	42	42	200	45	9
22 ^f	1.8	0.5	0.18	–	3.0	25	41	34	944	201	36
23 ^f	1.8	0.5	–	0.014	6.5	22	33	45	2080	642	57
24 ^f	1.8	0.5	0.18	0.014	6.5	11	26	63	2085	864	64

^a tof is equal to the value of ton has been reached in the first 1 h of reaction.^b Percentage of H₂O₂ has been consumed by the end of process.^c Acetic acid has been used instead of oxalic acid (3).^d Butyric aldehyde has been used instead of glyoxal (2).^e Oxidation has been carried out in the presence of 0.9 mol L⁻¹ of inhibitor.^f V₂O₅ has been used instead of VO(acac)₂ (1) (concentration by vanadium was the same as for the 1-based process).

of H₂O₂. Before distillation, all glassware was thoroughly rinsed with distilled water to remove any traces of metal). A saturated solution of vanadyl(IV)-acetylacetonate (95%, Aldrich) in acetonitrile was filtered through a microporous paper filter. Concentration of the filtrate at 40 °C in evaporator resulted in a solid which was dried under vacuum at 20 °C for 48 h. The final product, dark-green tiny (0.5–1 mm) crystals, was used in the oxidation experiments. Cyclohexane and solvents (acetonitrile, ethanol, glacial acetic acid (all of analytical grade)), vanadium(V)-oxide (98%, Aldrich), radical inhibitor (*N*-benzylidene-*tert*-butylamine, 98%, Aldrich), reducing agent triphenylphosphine (99%, Aldrich), catalase (3809 U/mg, Sigma–Aldrich) were used as purchased.

2.2. Oxidation reactions

The catalytic experiments were carried out at 40 °C in a round-bottom 25-mL glass flask reactor equipped with a reflux condenser and a magnetic stirrer. In a typical experiment, C₆H₁₂ (3.36 g, 1.8 mol L⁻¹) was mixed in the reactor with MeCN (15 mL), VO(acac)₂ (0.00032 g, 5 × 10⁻⁵ mol L⁻¹), glyoxal (0.232 g, 0.18 mol L⁻¹) and oxalic acid (0.038 g, 0.014 mol L⁻¹). After heating for 5 min under stirring, H₂O₂ (1.34 g, 1.8 mol L⁻¹) was injected, and this moment corresponded to the start of oxidation. Usually, the reaction was carried out for 5 h under atmospheric pressure.

2.3. Analysis of the reaction products

Samples have been withdrawn from the reaction mixture at regular intervals. The reaction samples were analyzed using either GLC Hewlett–Packard 5890, series II apparatus (flame-ionization detector, capillary column 30 m × 0.25 mm, immobile phase HP Innowax) or LKhM-80 (flame-ionization detector, packed column 3 m × 3 mm, immobile phase OV-17 on Chromaton N-AW). Prior to the analyses, *sec*-butylbenzene solution in ethanol was added

as internal standard to the withdrawn sample. The identification of the oxidation products was performed by comparison with the retention times of commercial cyclohexanol and cyclohexanone. Subsequently, both the conversion and the selectivity were determined by the common calculation procedure. The quantification of the oxygenated products was performed using a multi-points calibration curves. In order to determine the proper content of C₆H₁₁OH, C₆H₁₀O and C₆H₁₁OOH, each sample was analyzed by GC twice, before and after addition of triphenylphosphine (in the presence of PPh₃, C₆H₁₁OOH is quantitatively transformed into C₆H₁₁OH, then, its true content can be calculated as the difference between the C₆H₁₁OH concentration before and after PPh₃ addition) [17].

The GC–MS analysis of the oxidation products has been conducted on the Finnigan Trace MS 2000 Series apparatus.

Titration of the samples in the presence of KI using a 0.10 mol L⁻¹ aqueous solution of Na₂S₂O₃ allowed the determination of consumed H₂O₂.

The amount of glyoxal which had been consumed, was quantitatively determined after selective cleavage of the remained H₂O₂ using catalase. The mixtures are let for 12 h in the water buffers at pH 6.9–7.9 and 25 °C. Under such conditions, H₂O₂ is completely destroyed by the enzyme and the contents of 2 and 3 can be determined by titration using 0.02 mol L⁻¹ KMnO₄ at 70 °C [18].

3. Results and discussion

The oxidations of C₆H₁₂ have been carried out under an atmosphere of air using 1–10 equiv. of H₂O₂, a catalytic amount of 1 and various quantities of 2 and 3. As shown from the results collected in Table 1, all conditions led to a mixture of C₆H₁₁OH, C₆H₁₀O and C₆H₁₁OOH. These three components are produced simultaneously from the beginning of the reaction, regardless of the absence (Fig. 1) or presence (Fig. 2) of 2 and 3. With (1 or 5) × 10⁻⁴ mol L⁻¹ of 1 in

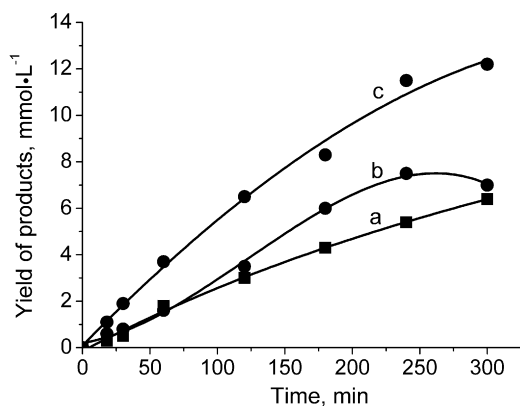


Fig. 1. The kinetics of product accumulation in the absence of activators. Oxidation conditions: $1.8 \text{ mol L}^{-1} \text{ C}_6\text{H}_{12}$, $5 \times 10^{-4} \text{ mol L}^{-1} \text{ VO}(\text{acac})_2$, $1.8 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, MeCN, 40°C . (a) $\text{C}_6\text{H}_{11}\text{OH}$, (b) $\text{C}_6\text{H}_{10}\text{O}$, (c) $\text{C}_6\text{H}_{11}\text{OOH}$.

MeCN, the conversion was no more than 1.6% (Table 1, Entries 1 and 7), but increased to about 4% in the presence of 0.18 mol L^{-1} of **2** (Entry 2), and to above 5% with 0.14 mol L^{-1} of **3** (Entry 5).

Moreover, the conversion could be improved to 7.6% by reducing the quantity of **3** to 0.045 mol L^{-1} (Entry 6). In the absence of an additive (compare Entries 1 and 3) or in the presence of **2** (Entries 2 and 4), the use of a very small amount of **3** (0.001 mol L^{-1}) has no effect on the conversion. Under similar conditions, switching from MeCN to EtOH as the solvent affords less than 1% conversion of alkane despite the presence or absence of additives.

In order to clarify how the catalyst and additives affect the oxidation process, subsequent experiments have been carried out in MeCN with different quantities of **1**, **2** and **3**. With $1 \times 10^{-4} \text{ mol L}^{-1}$ of **1**, the conversion increased from 0.7% in the absence of any additive (Entry 7) to 1.2% in the presence of 0.18 mol L^{-1} of **2** (Entry 8) and 4% with 0.014 mol L^{-1} of **3** as supplementary additive (Entry 9). Interestingly, a conversion as high as 7.2% with $\text{ton} = 2400$ was obtained with only $5 \times 10^{-5} \text{ mol L}^{-1}$ of **1**, if 0.014 mol L^{-1} of **3** was used together with **2** (Entry 10). Carrying out the reaction in the presence of an enhanced amount of **3** (Table 1, Entry 5; Fig. 3), comparable to the quantity of **2**, increased the conversion, yields and ton . However, there is an optimal content of **3**, between 0.011 and 0.022 mol L^{-1} as shown in Fig. 3. Exceeding this amount drops the alkane conversion and ton . This could be related to some coordination of the monoanion of **3** to vanadium; a similar effect has been reported with pyrazine-2-carboxylic acid [19,20]. Diminution of the oxidation efficiency caused by the excess of **3** could be

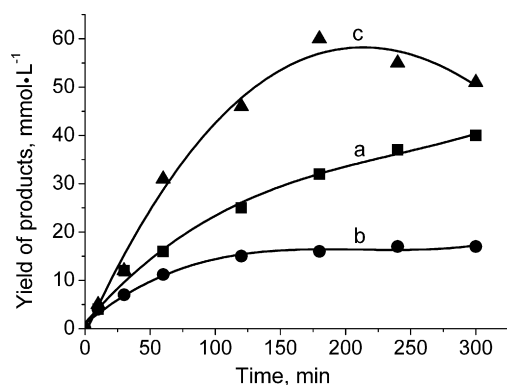


Fig. 2. The kinetics of product accumulation in the presence of activators. Oxidation conditions: $1.8 \text{ mol L}^{-1} \text{ C}_6\text{H}_{12}$, $5 \times 10^{-4} \text{ mol L}^{-1} \text{ VO}(\text{acac})_2$, 0.18 mol L^{-1} glyoxal, 0.014 mol L^{-1} oxalic acid, $1.8 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, MeCN, 40°C . (a) $\text{C}_6\text{H}_{11}\text{OH}$, (b) $\text{C}_6\text{H}_{10}\text{O}$, (c) $\text{C}_6\text{H}_{11}\text{OOH}$.

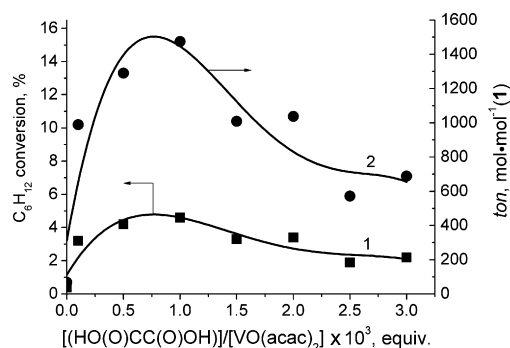


Fig. 3. Cyclohexane conversion (**1**) and process ton (**2**) as a function of the oxalic acid content. Oxidation conditions: $1.8 \text{ mol L}^{-1} \text{ C}_6\text{H}_{12}$, $5 \times 10^{-4} \text{ mol L}^{-1} \text{ VO}(\text{acac})_2$, $1.8 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, MeCN, 40°C , 5 h.

attributed to the acceleration of the heterolytic cleavage of H_2O_2 which would prevail over the homolytic one at very low pHs [21] ($\text{pH} = -2$ was reached in the case of high amounts of **3**).

Decreasing the C_6H_{12} concentration resulted in a noteworthy increase of the conversion (to more than 30%) with, simultaneously, acceptable ton , turnover frequency (tof), selectivity and efficiency E_c of H_2O_2 consumption. The last parameter can be calculated as the ratio $\text{C}_6\text{H}_{12} \text{ conversion} / \Delta\text{H}_2\text{O}_2$, where $\Delta\text{H}_2\text{O}_2$ is taken from the respective entries of Table 1 (for the Entries 13–16 the E_c values have reached 60–90%). Given these results, such procedure supports favorably the comparison with those already reported [7,19]. In solvent-free experiments or using solely O_2 as oxidant, only traces of oxidized products ($\leq 0.1\%$ conversion of C_6H_{12}) have been detected.

The presence of oxalic acid or glyoxal + oxalic acid increases also the relative amount of $\text{C}_6\text{H}_{11}\text{OOH}$ if **3** is taken in a very small concentration (Entries 3 and 4). Using low amounts of **3** with elevated concentration of cyclohexane led to cyclohexyl hydroperoxide as the major product even with the highest catalyst concentration. Further enhancing the oxalic acid amount from 0.001 (Entry 3) to 0.045 – 0.14 mol L^{-1} (Entries 5 and 6) decreases the $\text{C}_6\text{H}_{11}\text{OOH}$ yield and shifts the $\text{C}_6\text{H}_{11}\text{OH}/\text{C}_6\text{H}_{10}\text{O}$ ratio from 0.1–0.15 to 4–5. Carrying out the oxidation with acetic acid instead of **3** (Entry 17) does not lead to a notable improvement of the oxidation; compared to the acid-free process, the relative increase of conversion and ton was about 5–6%. Replacing glyoxal with butyric aldehyde (Entries 18 and 19) depresses the conversion and others parameters of the process as well (compare to Entry 10).

In order to investigate the mechanism, the influence of a hydroxyl radical scavenger, *N*-benzylidene-*tert*-butylamine (InH) [19] on the process has been studied. In the presence of this inhibitor, the cyclohexane conversion, selectivity, ton , and tof were notably reduced with simultaneous decrease of the $\text{C}_6\text{H}_{11}\text{OOH}/(\text{C}_6\text{H}_{11}\text{OH} + \text{C}_6\text{H}_{10}\text{O})$ ratio from 3.2 to 1.0 (compare Entries 10 and 20, Table 1). The last fact also points out that the bulk of the $\text{C}_6\text{H}_{11}\text{OOH}$ is generated by the free radical pathway. However, the reaction was not completely depressed, even when the InH amount exceeded the catalyst concentration by 50×10^3 times (Fig. 4, curve 1). The yield decreased from 150 mmol L^{-1} in the absence of InH to about 60 mmol L^{-1} when the value of inhibitor/catalyst molar ratio increased to $\sim 20 \times 10^3$. Subsequent increase of this ratio to 50,000 did not lead to change in the yields (Fig. 4, curve 1). Taking into account the peculiarities of oxidation in the presence of InH, one can consider that a noticeable amount of product is formed via a pathway which does not involve the participation of free radicals.

The oxidation of cyclohexane by H_2O_2 catalyzed with **1** led to modifications of the color of the reactive mixture which has been examined using UV spectra. Indeed, injection of H_2O_2 into a solu-

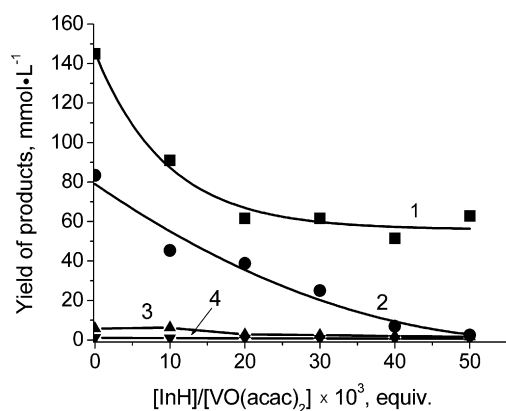


Fig. 4. The total yield of the desired products as a function of inhibitor/ $\text{VO}(\text{acac})_2$ molar ratio. Oxidation conditions: $1.8 \text{ mol L}^{-1} \text{ C}_6\text{H}_{12}$, $5 \times 10^{-5} \text{ mol L}^{-1} \text{ VO}(\text{acac})_2$, 0.18 mol L^{-1} glyoxal, 0.014 mol L^{-1} oxalic acid, $1.8 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, MeCN, 40°C , 5 h. 1, $\text{VO}(\text{acac})_2$ + glyoxal + oxalic acid; 2, $\text{VO}(\text{acac})_2$ + oxalic acid; 3, $\text{VO}(\text{acac})_2$ + glyoxal; 4, $\text{VO}(\text{acac})_2$.

tion of **1** causes almost instantaneous (2–10 s) transformation of the initial blue-green (depicted by broad absorption band located at 600–750 nm) color to intense yellow (inherent to the species absorb at $\lambda_{\text{max}} = 450 \text{ nm}$, Fig. 1S), then more slowly to grey-brown and very gradually back to greenish. Given the spectral data (Fig. 1S, inset), in about 20 s the yellow species evolve towards intermediates with $\lambda_{\text{max}} = 360 \text{ nm}$. Then both types of species gradually decayed without formation of any detectable intermediate. The literature indicates the color of various vanadium-containing species: VO_2^+ , yellow; VO^{2+} , blue; V^{3+} , green; V^{2+} , purple [22,23]. Thus the color changes can be related to the prevalence of these cations in the reaction mixture as well as to the presence of peroxy- and oxo-vanadium species [19,24]. By addition of **2**, the initial blue-green color of the mixture is preserved for a slight longer ($\sim 20 \text{ s}$) period. The shape of the spectra and their time-traces become also slightly different (compare the insets of Figs. 1S and 2S). Hence, one can make the assumption that **2** leads to some modification of **1**.

The addition of **3** into to the solution of **1** caused fast decolorization of the initial blue-green solution with decrease of the absorption at $\lambda_{\text{max}} = 330 \text{ nm}$ (Fig. 5); this was not observed in the case of the **1**+**2** interaction. This effect, which can be attributed to fast and strong ligation of the oxalate anion to vanadium [13] (as assumed using the PCA ligand [12,19,24]) was also observed in the case of Fe, Cr and Mn cations [23,25,26]. The existence of a clear isobestic point on the spectra of the **1**+**3** mixture after H_2O_2 addition (Fig. 6) argues for this assumption. The presence of even a catalytic amount of oxalic acid in a solution contain-

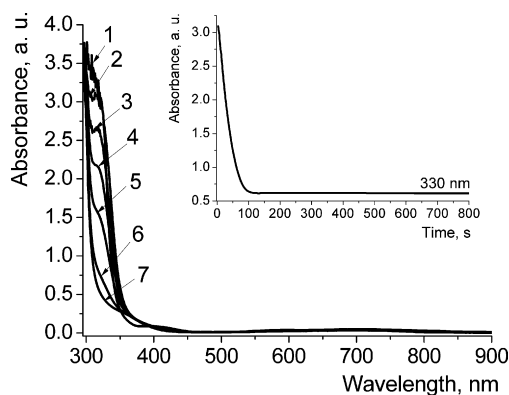


Fig. 5. The electronic spectrum of $5 \times 10^{-4} \text{ mol L}^{-1} \text{ VO}(\text{acac})_2$ in 2 mL MeCN (**1**) and spectra of the same solution taken at 5 s (**2**), 20 s (**3**), 30 s (**4**), 50 s (**5**), 70 s (**6**) and 90 s (**7**) respectively after 0.02 mmol of oxalic acid addition, 20°C . Inset: time-traces.

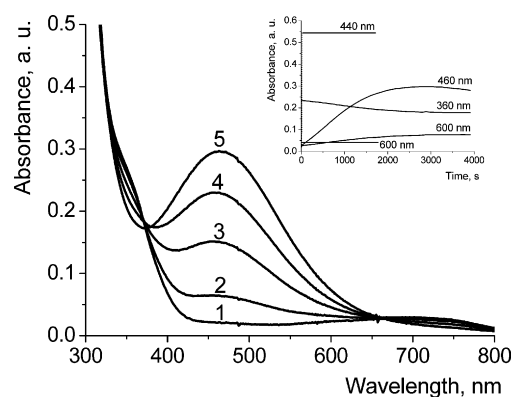
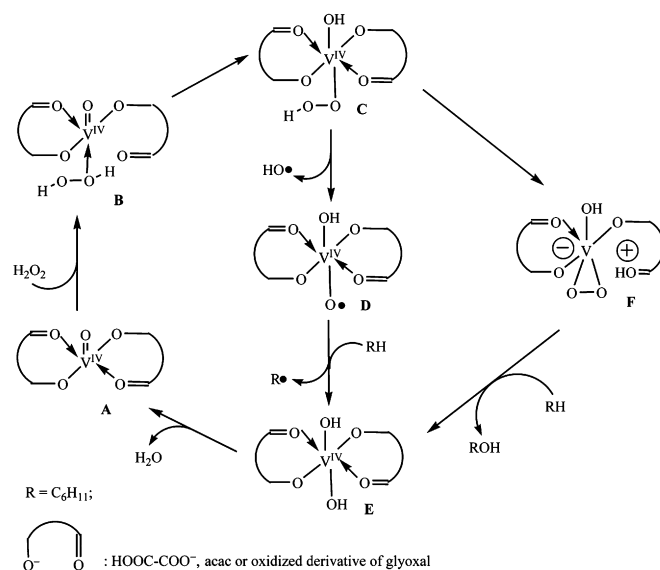


Fig. 6. The electronic spectrum of $5 \times 10^{-4} \text{ mol L}^{-1} \text{ VO}(\text{acac})_2 + 0.01 \text{ mol L}^{-1}$ oxalic acid mixture in 2 mL MeCN (**1**) and the spectra of the same solution taken at 250 s (**2**), 750 s (**3**), 1500 s (**4**) and 3000 s (**5**), respectively after injection of 0.03 mmol H_2O_2 , 20°C . Inset: time-traces (straight lines taken in the absence; curves, in the presence of oxalic acid).

ing **1** can preserve, for few hours, the appearance of the yellow color after H_2O_2 addition. As one can see, instead of very fast (less than 10 s in the absence of species absorbing at $\lambda_{\text{max}} = 440 \text{ nm}$ (corresponding to the yellow color) (Fig. 6, inset, straight line), the addition of oxalic acid noticeably prolongs the time of the green-blue color ($\lambda_{\text{max}} = 600 \text{ nm}$; Fig. 6, inset, curved line depicted absorption at $\lambda_{\text{max}} = 460 \text{ nm}$). Addition of **3** also preserved the conversion of species with $\lambda_{\text{max}} = 460 \text{ nm}$ into the ones absorbing at $\lambda_{\text{max}} = 360 \text{ nm}$ (compare the insets of Figs. 1S and 2S with the one of Fig. 6). The spectra modifications can result from the coordination of oxalate anion to the catalyst [19,22–24].

In order to compare of the catalytic activity of V^{4+} and V^{5+} cations under the designed conditions, the V_2O_5 -based process has been explored. In the V_2O_5 -catalyzed cyclohexane oxidation the formation of the desired products has been also detected (Table 1, Entry 21). The presence of additives significantly promotes their generation (compare Entry 21 with Entries 22–24) similarly to that using **1**-based experimental conditions. Consequently, we suspect that, under our conditions, V_2O_5 and $\text{VO}(\text{acac})_2$ led to analogous active oxidation species.



Scheme 1. The key steps of the putative mechanism of C_6H_{12} oxidation activated by oxalic acid.

The analysis of the amount of **2** at the end of the oxidation showed that this additive is partially consumed (30–40%). In respect to the products formed from **2**, the glyoxylic(H(O)CC(O)OH) and oxalic acid have been detected.

Taking into account the above experimental data, we suggest a mechanism involving the key steps depicted by Scheme 1. The process would occur via a radical pathway represented by $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow A$ [12,19,24,27], and a non-radical one illustrated by $A \rightarrow B \rightarrow C \rightarrow F \rightarrow E \rightarrow A$. The $F \rightarrow E$ transformation would involve interactions of cyclohexane at the second sphere coordination of F. Under our oxidation conditions, cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide would be generated simultaneously, with different rates, from the beginning of the oxidation process.

4. Conclusion

Given the above experimental data, it appears that the traditional free radical chain scheme of hydrocarbons oxidation ($C_6H_{12} \rightarrow C_6H_{11}OOH \rightarrow C_6H_{11}OH + C_6H_{10}O$) has to be complemented with a non-radical pathway. The practical interest of the above protocol lies in the use of commercially available relatively cheap low toxic reagents leading to an effective oxidation of cyclohexane with hydrogen peroxide at 40 °C under atmospheric pressure. The application of the acquired knowledge to the oxidation of others substrates, such as linear alkanes [27] is underway.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apcata.2010.10.010](https://doi.org/10.1016/j.apcata.2010.10.010).

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