

Studying on Liquid Phase Cyclohexane Oxidation Enhanced by Oxalic Acid: Pertinent Response by Long-Lasting Challenge

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A new effective protocol for oxidation of cyclohexane in acetonitrile at 40 °C and atmospheric pressure into cyclohexanol, cyclohexanone and cyclohexylhydroperoxide using H₂O₂ as sustainable oxidant, vanadyl(IV)-acetylacetonate as starting catalyst, oxalic acid and glyoxal as activating additives is presented with some reaction mechanism proposals.

Mild oxidation, cyclohexane, vanadyl(IV)-acetylacetonate, H₂O₂, oxalic acid, glyoxal, process activators, mechanism.

Introduction

Despite the extensive efforts aim to elaborate of new effective and energy-spared protocol for the cyclohexane oxidation the denoted problem remains one among the biggest challenges of contemporary chemistry. It refer to the extended application of oxidized products, i.e. cyclohexanol, cyclohexanone and cyclohexylhydroperoxide as precursors in artificial fibers industry (Nylon 6 and 6,6). 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 [1]. On the other hand, what is even more important, study by activation the extraordinary strong C—H bonds of C₆H₁₂ (BDE = 98 kcal mol⁻¹) would result in new fundamental knowledge be useful for elaboration the modern methods of others industrially-meaningful substrates functionalization. The actual study reports that the VO(acac)₂ (**1**) catalyzed cyclohexane oxidation by H₂O₂ at mild conditions is notably improved by using both glyoxal and it oxidized descendant oxalic acid (**3**). The putative mechanism the denoted additives influence is elucidated by GLC, UV-Vis, CV, EPR, ESI-MS.

Kinetics and mechanism of C₆H₁₂ oxidation in presence of glyoxal and oxalic acid

In the absence of **2**, the reaction of C₆H₁₂ with H₂O₂ (1 equiv.by substrate) at 40 °C

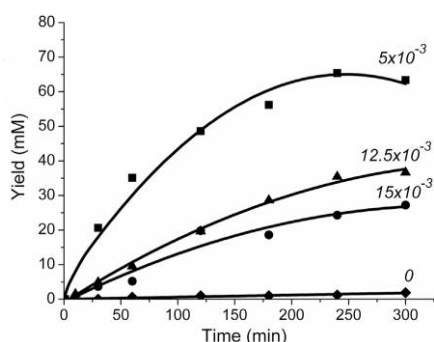
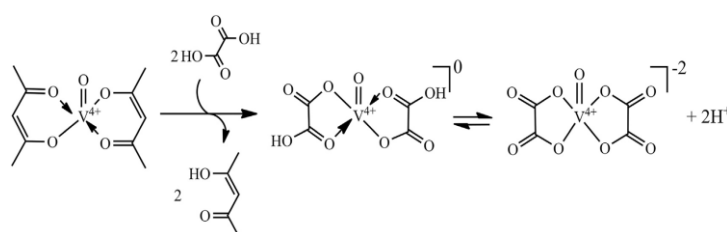


Fig. 1. Kinetics of sum products accumulation. Concentration of **2** is given in M above of each curve.



Scheme 1. The plausible structures of **1+2** interaction.

requires at least $(0.3\div0.6)\times10^{-3}$ M of **1** to generate the detectable amounts of products – $C_6H_{11}OH$, $C_6H_{10}O$ and $C_6H_{11}OOH$ (Fig. 1). Below of this range the yield of aimed products was ignorable (curve 1, Fig. 1) and the level of H_2O_2 utilization (ΔH_2O_2) and its effectiveness ($Eff_{H_2O_2}$) was $<1\%$ and $>90\%$, respectively (Table 1). The addition of **2** into the reaction mixture contained even 0.06 mM of **1** resulted in a four-fold increasing of cyclohexane conversion (even in respect to the 10 times higher catalyst concentration of **2**-free experiment) concomitant with the $Eff_{H_2O_2}$ growing (entries 2 and 7, Table 1). Simultaneous decreasing the catalyst and substrate initial load (Table 1, entries 4 and 8) lead to enhancing the conversion, turnover number (TON), and process efficiency from 5% (entry 4) to 30% (entry 8) and $Eff_{H_2O_2}$ from 8% to 16%, respectively. Due to the instrumental analysis the initial **1** as well as the originated in situ $VO(oxalate)_2$ (Scheme 1, Fig. 2, 3) can interact with H_2O_2 produce the $VO(\eta-O)_2$ -based species.

Table 1. The effect of **2** additives in **1**-catalyzed cyclohexane oxidation.^a

Entry	1 $\times 10^3$, M	2	ΔC_6H_{12} %	Selectivity, mol%			TON	$\Delta H_2O_2^b$, %	$Eff_{H_2O_2}^c$, %
				$C_6H_{11}OH$	$C_6H_{10}O$	$C_6H_{11}OOH$			
1	0.06	-	<0.1	-	-	-	-	<1	>90
2	0.6	-	1.2	33	62	5	23	48	4.2
3	0.6	1.0	1.7	1	8	91	51	52	6.5
4	0.6	15	5.3	48	7	45	169	96	8.4
5	0.6	50	7.6	43	13	44	253	90	13.2
6	0.6	150	5.2	47	10	43	173	80	9.9
7	0.06	50	5.1	23	25	43	1516	25	32.4
8 ^d	0.06	15	30	22	44	34	944	34	15.7
9 ^e	0.06	30	0.2	29	29	42	56	5	6.8

^a $[C_6H_{12}]_0 = [H_2O_2]_0 = 1.8$ M; $[VO(acac)_2]_0 = 0.06 \times 10^{-3}$ M. MeCN, 40°C, 5 h. (For all catalytic tests, the products selectivity was above 90%). ^bAmount of H_2O_2 consumed. ^c $Eff_{H_2O_2}$ is the ratio of stoichiometric (by products yield) amount of H_2O_2 divided by the H_2O_2 consumed. ^d $[C_6H_{12}]_0 = 0.18$ M. ^eAcetic acid has been used instead of **2**. The ΔC_6H_{12} (substrate conversion) values match well with the products yield due to the almost 100% process selectivity.

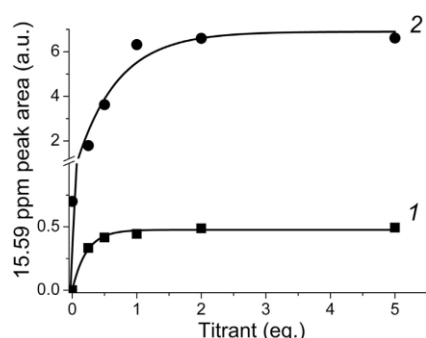


Fig. 2. Kinetics of enol OH peak (15.59 ppm) growing during of **1** (1.5×10^{-3} M) solution titration by H_2O_2 (**1**) and **2** (**2**), CD_3CN , 20 °C.

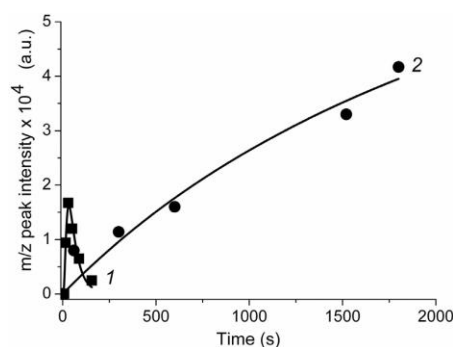


Fig. 3. Time-traces of $[VO(\eta-O)_2(acac)]^+$, m/z 198.981 (**1**) and $[VO(\eta-O)_2(oxalate)]^-$, m/z 186.908 (**2**) species accumulation.

Conclusion

Privilege formation of $VO(\eta-O)_2$ species in **1** + **2** oxidation is responsible for the revealed effect.

[1] J. O. Metzger, M. Eissen, "Concepts on the contribution of chemistry to a sustainable development. Renewable raw materials", *C. R. Chimie*, 7, pp. 569-581, 2004.