Molecular Catalysis 434 (2017) 194–205

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

MCAT

V(IV)-catalyzed cyclohexane oxygenation promoted by oxalic acid: Mechanistic study

Alexander Pokutsa[a,*], Yulia Kubaj[a], Andriy Zaborovskyi[a], Dariya Maksym[a], Tomasz Paczesniak[b], Bogdan Mysliwiec[b], Ewa Bidzinska[c], Jacques Muzart[d], Andrzej Sobkowiak[b]

[a] *Department of Physical Chemistry of Combustible Fossils NAS of Ukraine, Institute of Physical Organic Chemistry and Chemistry of Coal NAS of Ukraine, Naukova Str., 3A, Lviv 79060, Ukraine*
[b] *Rzeszow University of Technology, P.O. Box 85, 35-959 Rzeszow, Poland*
[c] *Jagiellonian University, Institute of Chemistry, P.O. Box 30-060, Ingardena Str., 3, Krakow, Poland*
[d] *CNRS – Université de Reims Champagne-Ardenne, Institut de Chimie Moléculaire de Reims, UMR 7312, UFR des Sciences Exactes et Naturelles, BP 1039, 51687 Reims Cedex 2, France*

ARTICLE INFO

Article history:
Received 25 November 2016
Received in revised form 17 January 2017
Accepted 9 February 2017

In memory of doctor Petro I. Pokutsa.

Keywords:
Cyclohexane oxygenation
Hydrogen peroxide
Vanadyl(IV)acetylacetonate
Oxalic acid
Mechanism

ABSTRACT

Study the mild cyclohexane oxygenation using vanadyl(IV)acetylacetonate as the starting catalyst and H_2O_2 as the oxidant has shown that oxalic acid as activator alters the products ratio, increases yield and catalyst turnover number. According to the instrumental (ESI-MS, NMR, EPR, UV–vis, GC, pH, titrimetric) investigations both the parental VO(*acac*)$_2$ and originated in situ vanadyl(IV)oxalate can consequently interact with H_2O_2 led, among others, to intermediates comprise $VO(\eta^2\text{-}O_2)$ metal core. Such vanadium-peroxo species manifest itself as the additional oxygenation agent which generation is inspired by oxalic acid additives. The enhanced aimed products yield and improved process selectivity revealed in the presence of oxalic acid may be stipulated with these non-radical intermediates.

1. Introduction

Study selective cyclohexane oxidation is important from both practical and theoretical points of view and still challenges science and technology [1]. Nowadays, it is a base process for cyclohexanol and cyclohexanone interim products manufacturing. The last ones are used to be a feedstock for as much as 2.3×10^6 T adipic acid and 4.4×10^6 T ε-caprolactam production annually [1c,d]. However, the worldwide commercial homogeneous Co(II)-catalyzed process, using air as an oxidant, is characterized by low (4–6%) cyclohexane conversion and moderate (75–80%) selectivity for $C_6H_{11}OH + C_6H_{10}O$. These shortcomings are attributed to the free-radical reaction mechanism, which takes place under severe conditions (160–180 °C, 1.3–1.5 MPa) the industrial process is carried out. In contrast, the efficient and almost 100% selective oxidation of organic substrates occurs in Nature at ambient temperature and pressure [2]. Such outstanding output is accomplished by the enzymes that efficiently activate dioxygen or hydrogen peroxide without free radicals involvement [2a,b]. Similarly, the high selectivity in such transformations manifested by artificial bio-inspired catalysts was assigned to its ability to ensure non-radical or hidden-radical pathways in C—H bond functionalization [2c–g]. Such approaches would be particularly beneficial in application to cyclohexane oxygenation because of extraordinary high value the C—H bond dissociation energy, BDE (98 kcal mol^{-1}) [3]. On the other hand, given the high price of sophisticated synthetic catalysts and specific reaction conditions to be maintained, the search for commercially applicable oxidation catalysts seems to be continued.

Previously we have reported that C_6H_{12} oxidation in the presence of VO(*acac*)$_2$ (**1**) can be notably enhanced by small amounts of oxalic acid (**2**) [4a]. The process kinetics and products yields were substantially depended on the relative permittivity ε_r and the redox properties of the reaction mixture [4b]. These observations prompted us to get more insight the mechanism of VO(*acac*)$_2$-catalyzed cyclohexane oxidation and elucidate the influence of oxalic acid as well.

---

* Corresponding author.
E-mail address: apokutsa@ukr.net (A. Pokutsa).

http://dx.doi.org/10.1016/j.mcat.2017.02.013

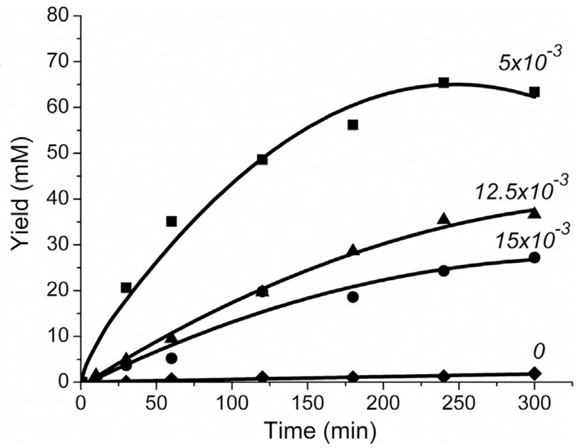


Fig. 1. The kinetic of the sum products ($C_6H_{11}OH + C_6H_{10}O + C_6H_{11}OOH$) accumulation. *Reaction conditions:* $[C_6H_{12}]_0 = [H_2O_2]_0 = 1.8$ M, $[VO(acac)_2]_0 = 0.06 \times 10^{-3}$ M, MeCN, 40 °C. Oxalic acid concentration (M) is printed above the respective curve.

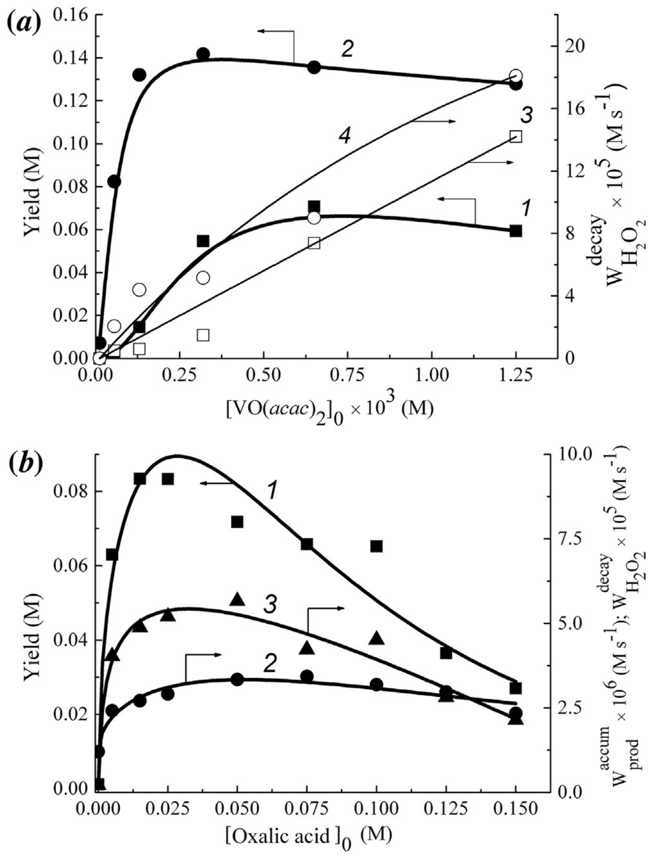
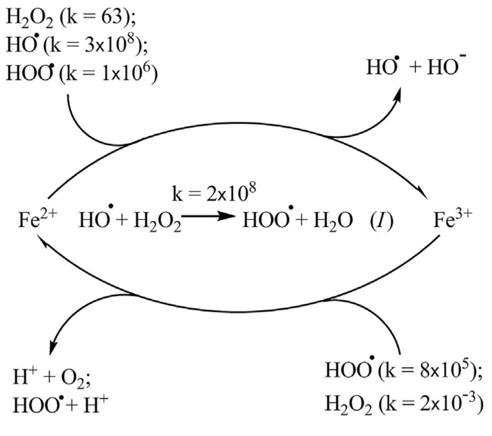


Fig. 2. Yield of products (*1, 2, 5*), initial rate ($W_{H_2O_2}$) of H_2O_2 consumption (*3, 4, 6*) and initial rate of products accumulation, W_{prod} (*7*) in dependence of $VO(acac)_2$ (a) and oxalic acid (b) starting concentration. Curves *1, 3* and *2, 4* are related respectively to the **1**- and **1** + **2**-based process. *Reaction conditions:* $[C_6H_{12}]_0 = [H_2O_2]_0 = 1.8$ mol L^{-1}, [oxalic acid]$_0 = 0.015$ mol L^{-1} (a), $[VO(acac)_2]_0 = 0.06 \times 10^{-3}$ mol L^{-1} (b); MeCN, 40 °C, 5 h.



Scheme 1. The set of key steps of Fenton cycle. Values of *k* (in M^{-1} s^{-1}) were adopted from [15].

2. Results and discussion

2.1. Kinetics of C_6H_{12} oxygenation in presence of oxalic acid

In the absence of **2**, the reaction of C_6H_{12} with H_2O_2 (1 equiv. by substrate) at 40 °C for 5 h requires at least $(0.3 \div 0.6) \times 10^{-3}$ M of **1** to generate the detectable amounts of products – $C_6H_{11}OH$, $C_6H_{10}O$ and $C_6H_{11}OOH$ (no adipic acid or caprolactam were discovered upon overall tested experimental conditions) (Figs. 1 and 2). Below of this range (e.g. at 0.06×10^{-3} M) the yield of aimed products was ignorable (curve *1*, Fig. 1) and the level of H_2O_2 utilization (ΔH_2O_2) and it effectiveness ($\mathrm{Eff}_{H_2O_2}$) was <1% and >90%, respectively (Table 1). Ten-folder increasing the $VO(acac)_2$ concentration led to rather modest improving in the yield and lifted the ΔH_2O_2 value to approx. 4% (entry 2, Table 1). However, the addition of **2** into the reaction mixture contained even so tiny amount of **1** (0.06 mM) 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 $\mathrm{Eff}_{H_2O_2}$ growing (compare entries 2 and 7, Table 1). Thus one can deduce that by simultaneous decreasing the catalyst and substrate initial concentrations (Table 1, entries 4 and 8), the conversion, turnover number (TON), and process efficiency (regarding of H_2O_2 consumed) can be enhanced. For example, lowering the C_6H_{12} concentration from 1.8 M to 0.18 M improves the cyclohexane conversion from approx. 5% (entry 4) to 30% (entry 8) and $\mathrm{Eff}_{H_2O_2}$ from 8% to 16%.

Presence of oxalic acid affects not only cyclohexane conversion but also the $C_6H_{11}OH$, $C_6H_{10}O$ and $C_6H_{11}OOH$ products ratio. The last factor was, in fact, not constant and varied in the course of process (Fig. S1a–d) because of $C_6H_{11}OOH$ catalytic decay to $C_6H_{11}OH$ and $C_6H_{10}O$. For instance, the discussed ratio was changed from 7/12/1 in the acid-free process (entry 2) to 1/8/90 when **2** presented in a small amount (entry 3). Further increasing of **2** content diminished the relative amount of cyclohexylhydroperoxide made the products ratio equal 4/1/4 (compare entry 3 with 4, 5 and 6). Decreasing of C_6H_{12} initial concentration causes similar declining in $C_6H_{11}OOH$ yield, changes the product ratio to 1/2/1.5 in spite of oxalic acid additives (compare entry 6 with 8 of Table 1 and Fig. S1b with S1c). Last fact was referred to the much lower rate of radical propagation step *XII* (Scheme 3a) stipulated by the lesser substrate content. In opposite, high catalyst concentration increases the yield of $C_6H_{11}OOH$ points out the free radical transformation of substrate (collate Fig. S1d with S1a–c). Reducing the relative amount of $C_6H_{11}OOH$ in the products profile indicates partial elimination of the free radical steps from the overall process mechanism [5]. Smaller molecular volume, higher charge on vanadium atom and ionization potential of $VO(oxalate)_2$ (**3**) compare to $VO(acac)_2$ (Table S1) designates the higher, compare to **1**, electrophilicity of **3**. This feature can be responsible for the benefit revealed in the presence of **2** additives as it was observed upon influence another steric, electronic, and stereo-electronic effects [2][2d,g].

The optimal (with respect to the products yield) concentration of **2** in the initial reaction mixture was $0.01 \div 0.050$ M (Fig. 2). Below of this level oxalic acid does not substantially affect the rate, conver-