

Benign Homogeneous Catalytic Oxidation of Cyclohexane Promoted with Glyoxal¹

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Received July 22, 2005

Abstract—Evidence of the promoted effect of dialdehyde (glyoxal) in $\text{VO}(\text{acac})_2$ - and $\text{Co}(\text{acac})_2$ -catalyzed oxidations of cyclohexane by H_2O_2 under ambient conditions is reported. The V-process leads to a mixture of cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide and TON up to 4400. The Co-process is much less active but leads selectively to cyclohexyl hydroperoxide. Glyoxal significantly accelerates the process rate and enhances the yield of desired products.

DOI: 10.1134/S0023158407010041

1. INTRODUCTION

Oxidation of alkanes is nowadays an important bulky industrial process and affords widely used products [1]. Due to the accessibility of feedstock and the relative stability and low-toxicity of saturated hydrocarbons, improvement of methods is constantly under way [2, 3].

The main part of cyclohexanone (**cO**) and cyclohexanol (**cOH**), which are the raw materials for the production of caprolactam and adipic acid, are obtained by the bulky oxidation of cyclohexane (**cH**) by O_2 /air catalyzed with soluble cobalt salts [3–5]. The free-radical mechanism of this process, caused by severe conditions (160–180°C), prevents reaching higher than 4–6% conversion in order to sustain the technologically acceptable selectivity (75–80%). Numerous efforts directed to improve this reaction still have not resulted in a process better than the contemporary commercial one. Up to the present, the proposed processes require operating with highly diluted mixtures of hydrocarbon in toxic and volatile solvents [6, 7] or using expensive oxidants [8] and exotic catalysts [9] in order to maintain both conversion and selectivity at a reasonable level.

A way to accelerate the reaction is to use promoters, the most familiar ones being aliphatic and aromatic mono-aldehydes [10]. In our efforts to find other promoters, we undertook systematic studies of the influence of a dialdehyde, glyoxal, on the VO^{2+} - and Co^{2+} -catalyzed oxidation of **cH** by hydrogen peroxide in an acetic acid medium. The advantage of glyoxal is its cheapness, nontoxicity, and low volatility. As for H_2O_2 , it has broad applications in oxidation processes [11], a

relatively low price, and the formation of only water as waste.

Commercially available vanadyl(IV)acetylacetone, $\text{VO}(\text{acac})_2$, and cobalt(II)acetylacetone, $\text{Co}(\text{acac})_2$, were selected as catalysts, since they are conventionally used in industrial processes that include bulk **cH** oxidation [12].

Preliminary results on this research have been published in [13]. The presented paper reports further spectroscopic and kinetic studies of this process.

2. EXPERIMENTAL

2.1. General Procedure

All reactions were performed in a 50-ml round-bottom two-neck glass flask equipped with water-jacketed reflux condenser and outlet/inlet port, placed in a silicon heating bath. Agitation was performed with a Teflon-coated round-shaped magnetic stirrer bar.

Probes of oxidates were analyzed on an HP-5890 series II FID gas chromatograph with a 3394A Integrator using an HP-Innowax 30 m, i.d. = 0.25 mm column and utilized a 1 : 100 split ratio. Ethanol was chosen as the internal standard due to its ability to stop the reaction evolution in the probe's vial. The structure of the products was determined from comparison to known compounds and by GS-MS (Finnigan Trace MS 2000 Series).

TLC-analysis was performed on Merck Silica gel 60 F_{254} plates (eluant: toluene/ethyl acetate 1/1; developer: 10% solution of phosphomolybdic acid in ethanol containing a few drops of H_2SO_4 , or saturated solution of NaI in acetone).

UV/Vis spectra were carried out on UVIKON 941 Plus two-beam Kontron Instruments in a 1-cm quartz

¹ This article was submitted by the authors in English.

Table 1. Glyoxal promoted homogeneous catalytic cyclohexane oxidation under O₂ and air^a

Entry	Reaction atmosphere	Mixture composition		Conv., %	Selectivity, %			TON	H ₂ O ₂ consumed, %
		Catalyst, μmol	H ₂ O ₂ , mmol		cO	cOH	cOOH		
VO(acac) ₂									
1 ^b	Air	0.5	28	5.9	13	41	46	3040	60
2	O ₂	8	14	3.6	28	52	20	125	97
3	Air	8	14	3.5	27	50	33	120	93
VO(acac) ₂ + glyoxal									
4 ^b	Air	0.5	28	7.2	16	35	49	4400	71
5	O ₂	8	14	4.9	34	39	27	170	98
6	Air	8	14	4.5	35	52	13	160	97
7 ^c	Air	8	28	5.9	15	41	23	460	92
CO(acac) ₂									
8	Air	8	14	0.5	0	1	99	17	19
9	O ₂	8	14	0.6	0	1	99	18	18
Co(acac) ₂ + glyoxal									
10	Air	8	14	1.0	0	2	98	35	43
11	O ₂	8	14	1.1	0.3	1.7	98	36	46

^a Cyclohexane (28 mmol), acetic acid (14 ml), glyoxal (5 ml), 40°C, 1 atm, 30 min; Air, O₂—reaction carried at ambient atmosphere (air) or bubbling of dioxygen (O₂) (20 ml min⁻¹).

^b Reaction time, 180 min.

^c *i*-Butyraldehyde (5 mmol) was used instead of glyoxal; reaction time, 60 min.

cuvette at room temperature. Kinetics of H₂O₂ consumption was monitored with titration of probes by 0.1 N KMnO₄. For this analysis 0.5 ml of the probe was placed in a conical flask containing 50 ml water and 1 ml concentrated H₂SO₄ and titrated under vigorous stirring.

2.2. Materials

Glacial acetic acid, cyclohexane, *i*-butyraldehyde, vanadyl(IV)acetylacetone, and cobalt(II)acetylacetone were obtained from ACROS and used as received. Triphenylphosphine (Jansen) and 2,6-*tert*-butyl-4-methylphenol (InH) (Aldrich) were used as purchased.

A 35% aqueous solution of hydrogen peroxide (Aldrich) and 30% aqueous glyoxal (Fluka) were concentrated by evaporation of water under vacuum, the first one to 70% (determined by titrimetry) and the second one to 45% (determined by volumetry).

2.3. Typical Reaction Procedure

A stirred mixture of cyclohexane (28 mmol), glyoxal (0–5 mmol), and 0.5–8 μmol of the catalyst in acetic acid (14 ml) was heated to 40°C under ambient atmosphere or with argon bubbling. After 5 min, the

zero probe was withdrawn; then 1.0 ml of an AcOH solution containing H₂O₂ (28 mmol) was injected into the reaction vessel. Probes of the reaction mixture were then withdrawn at regular intervals, mixed with the internal standard, and analyzed by GC twice—before and after addition of Ph₃P in order to establish the proper content of cO, cOH, and cyclohexyl hydroperoxide (cOOH) [11]. The quantification of the oxygenated products was obtained using a multipoint calibration curve for each product.

3. RESULTS AND DISCUSSION

The oxidation of cyclohexane by H₂O₂ with catalytic amounts of VO(acac)₂ and glyoxal in AcOH at 40°C and atmospheric pressure resulted with TON up to 4400 (Table 1). Under the same conditions, Co(acac)₂ was less efficient (Table 1). Oxidation products have been detected only in the presence of catalysts. The distribution of products was dependent on the nature of the catalyst cation. In the case of VO(acac)₂, cOH, cO, and cOOH were detected together in the beginning period of the reaction regardless of the reaction atmosphere (Tables 1, 2). In contrast, with Co(acac)₂, cOOH was the only product detected during

Table 2. Glyoxal promoted homogeneous catalytic cyclohexane oxidation under argon^a

Entry	Mixture composition		Conv., %	Selectivity, %			TON	H_2O_2 consumed, %
	Catalyst, μmol	H_2O_2 , mmol		cO	cOH	cOOH		
$\text{VO}(\text{acac})_2$								
1	4	28	4.4	13	44	43	310	44
$\text{VO}(\text{acac})_2 + \text{glyoxal}$								
2 ^b	0.5	28	7.1	16	38	46	4000	73
3 ^c	1	28	7.7	21	37	42	2200	83
4	4	28	6.9	34	49	17	485	92
$\text{CO}(\text{acac})_2$								
5 ^d	8	28	3.9	7	19	74	135	51
$\text{Co}(\text{acac})_2 + \text{glyoxal}$								
6 ^d	8	28	4.1	11	22	67	145	61

^a Cyclohexane (28 mmol), acetic acid (14 ml), glyoxal (5 ml), stirring at 40°C under bubbling of argon (20 ml min⁻¹), 30 min.^{b, c, d} Reaction times, 180, 60, and 360 min, respectively.

the beginning period. Adipic acid was found in trace amounts.

The detection of cOOH, in all cases as soon as the reaction started, indicates that the process involves the formation of radicals. In agreement with this assumption, the yield of the products and their composition as well as the kinetics of their accumulation depend on the presence of free radical inhibitors (Figs. 1, 2).

Indeed, 2,6-*tert*-butyl-4-methylphenol (InH) increased the induction period and hampered the cH

transformation. According to the results depicted in the Tables 1 and 2 and Fig. 3, cO and cOH were being accumulated with significant amounts of cOOH. This fact is in some discrepancy from the information provided in [15, 16] despite the similarity of the catalytic systems; this is obviously due to differences in the methodology of product detection.

To determine the possible influence of oxygen on the process rate and mechanism, cH was oxidized

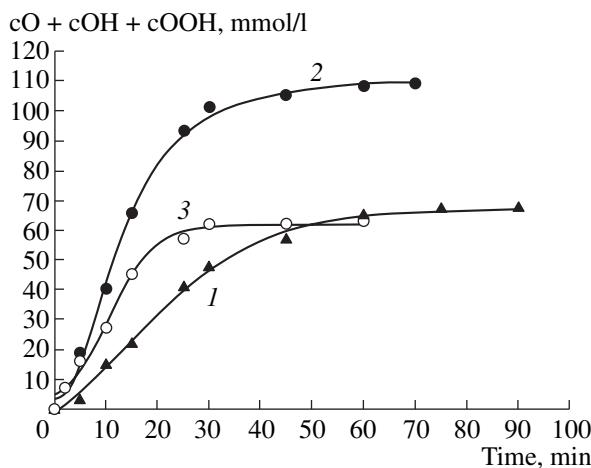


Fig. 1. The kinetics of total cO + cOH + cOOH accumulation during cH oxidation. 28 mmol cH, 28 mmol H_2O_2 , 1 μmol $\text{VO}(\text{acac})_2$, AcOH, 40°C. Filled triangles— $\text{VO}(\text{acac})_2$, glyoxal (5 mmol), InH (0.1 mmol), air; filled circles— $\text{VO}(\text{acac})_2$, glyoxal (5 mmol), Ar; open circles— $\text{VO}(\text{acac})_2$, Ar.

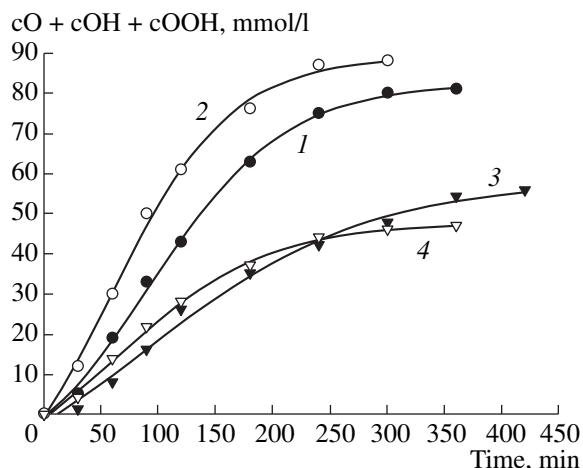
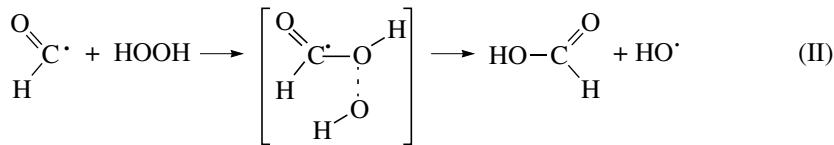
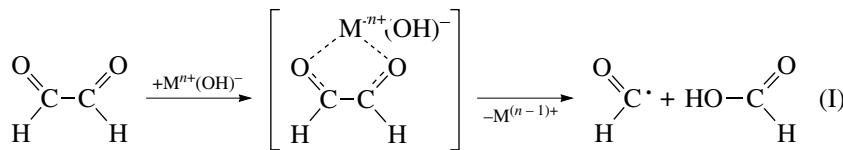


Fig. 2. The kinetics of total cO + cOH + cOOH accumulation in dependence on the reaction atmosphere and presence of dialdehyde. 28 mmol cH, 28 mmol H_2O_2 , 8 μmol $\text{Co}(\text{acac})_2$, AcOH, 40°C. Filled circles—Ar atmosphere; open circles—air atmosphere, glyoxal (5 mmol); filled triangles—Ar atmosphere; open triangles—air atmosphere, glyoxal (5 mmol), InH (0.1 mmol).



$$\begin{aligned}
 \text{M}^{n+} &= \text{V}^{5+}, \quad \text{M}^{(n-1)+} = \text{V}^{4+}; \\
 D_{\text{H-OORH}} &\approx D_{\text{H-ROOH}} = 90 \text{ kcal/mol}, \quad D_{\text{HO-OH}} = 50 \text{ kcal/mol} \quad [20]
 \end{aligned}$$

Scheme 1.

under the ambient atmosphere, as well as with oxygen (Table 1) and argon (Table 2) bubbling.

No noticeable difference in the rates of the process or features of goal products accumulation depending on the reaction atmosphere were determined when the process was catalyzed with $\text{VO}(\text{acac})_2$ (Tables 1, 2). With $\text{Co}(\text{acac})_2$ as the catalyst, the presence of oxygen benefits slightly the product yield (Fig. 2). These data (low susceptibility to O_2 and partial suppression of oxidation by a free-radical inhibitor) coincide with the previous conclusion [17] that two mechanisms occur, radical and nonradical, for these types of catalytic system.

A reciprocal transformation of color of the $\text{VO}(\text{acac})_2$ in AcOH solution from green (V^{4+}) to yel-

low-brown (V^{5+}) after addition of H_2O_2 and spontaneously back have been visually observed and recorded with the UV/Vis spectrometer (Fig. 4).

In contrast, samples of $\text{Co}(\text{acac})_2$ after treatment with H_2O_2 displayed only one-way transformation of their color from pink (Co^{2+}) to green (Co^{3+}) (Fig. 5).

The observed spectrometric effect can be related to the differences in the redox potentials (E^0) of cations and hydrogen peroxide. As $E^0(\text{V}^{4+}/\text{V}^{5+}) = 1.00 \text{ V}$ [18] is much lower than $E^0(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.77 \text{ V}$ [19], it benefits the fast oxidation of V^{4+} to V^{5+} species by H_2O_2 . At the same time, E^0 for $(\text{Co}^{2+}/\text{Co}^{3+})$ is 1.83 V [18]. Hence, due to the similarity of the redox potentials of hydrogen peroxide and the cobalt(II)/(III) cation, the rate of oxi-

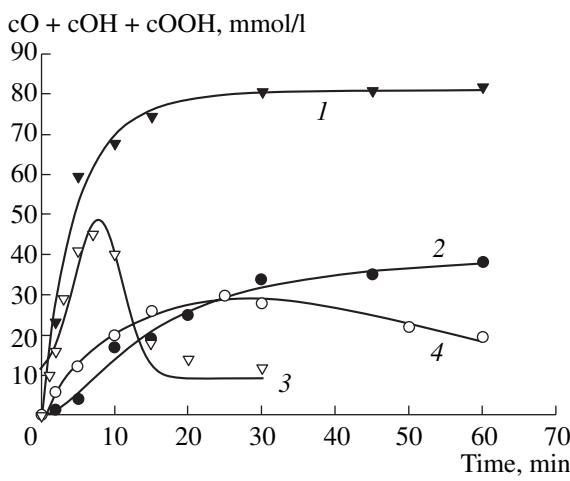


Fig. 3. The kinetics of $\text{cO} + \text{cOH}$ (1, 2) and cOOH (3, 4) accumulation during ch oxidation. 28 mmol ch , 28 mmol H_2O_2 , 4.0 μmol $\text{VO}(\text{acac})_2$, AcOH , 40°C , Ar. (2, 4)—without glyoxal; (1, 3)—with 5 mmol glyoxal.

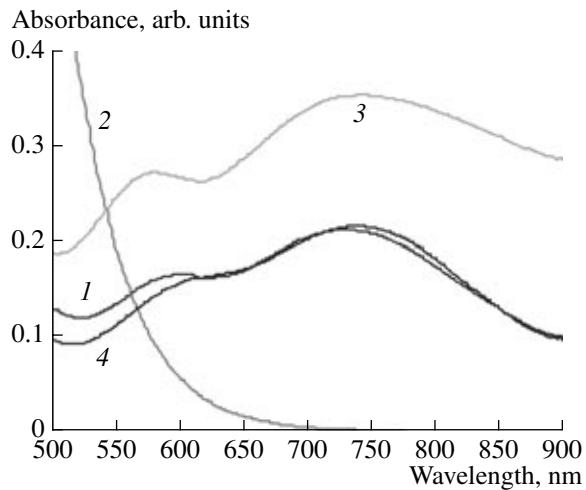


Fig. 4. UV/Vis spectra of the solution of $\text{VO}(\text{acac})_2$ (13 mmol/l) in AcOH recorded at various moments of its treatment with 70% H_2O_2 (5 mg): (1) 0, (2) 5, (3) 15, and (4) 30 min.

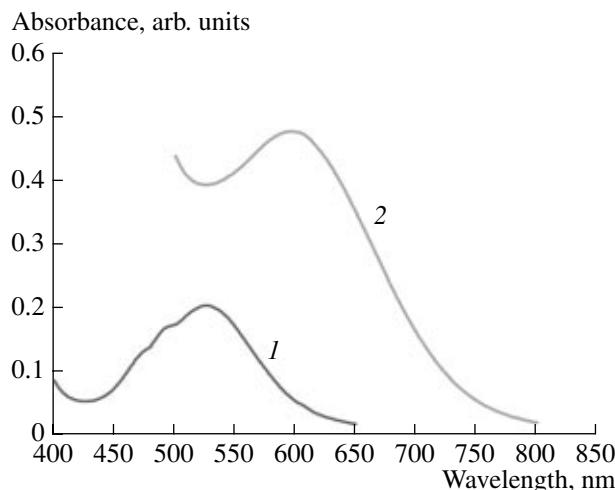


Fig. 5. UV/Vis spectra of the solution of $\text{Co}(\text{acac})_2$ (13 mmol/l) in AcOH recorded at various moments of its treatment with 70% H_2O_2 (5 mg): (1) 0 and (2) 5 and 10 min.

dation as well as the reduction of the later by H_2O_2 is relatively hampered. At the present time, we cannot explain the spontaneous change in color for V-assisted decomposition of H_2O_2 in AcOH . A feasible reaction among high-valent vanadium-oxo species and acetic acid followed with peracetic acid formation also cannot be ruled out.

The subsequent addition of a new portion of H_2O_2 for the vanadium-catalyzed process recommenced the cH oxidation with the same rate (Fig. 6). A significantly lower effect on product enhancing was developed with such an addition of H_2O_2 for the Co-catalyzed reaction.

The high activity of the vanadium catalyst under the conditions of the present process can be explained by the coordination of hydrogen peroxide on the V^{IV}O core [20] followed by the fast cleavage of the O–O bond that releases hydroxyl radicals and probably high-valent V^{V} -oxo species. The role of glyoxal can consist in the formation with salts of transition metals of $[\text{C}_2\text{H}_2\text{O}_2\text{--M}^{n+}]$ intermediates [18] followed by their decomposition. Hence, the oxidized form of the V-catalyst can be reduced by glyoxal according to step **I** (Scheme 1) that leads to formation of HCO^\cdot -radicals. The alkyl-oxy radicals by step **II** can easily react with hydrogen peroxide to produce the additional amount of hydroxyl-radicals. The later ones (also formed in the Haber–Weiss cycle [22]) are responsible for the process rate acceleration.

The effect of both the nature of the catalyst and the promoter on the process implies differences in the reactive intermediates presented in the reaction mixture.

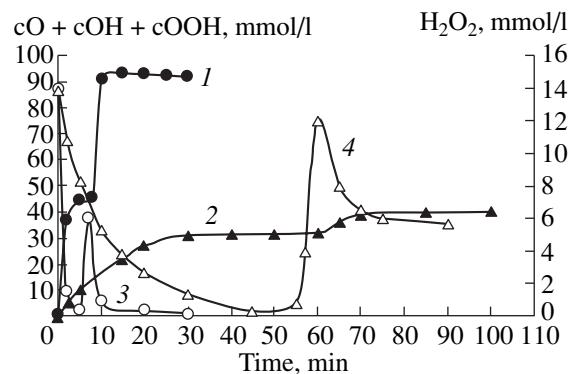


Fig. 6. The kinetics of total $\text{cO} + \text{cOH} + \text{cOOH}$ (1, 2) formation and H_2O_2 (3, 4) consumption in dependence on the nature of the catalyst. 14 mmol H_2O_2 injection after 10 min ($\text{VO}(\text{acac})_2$) or 60 min ($\text{Co}(\text{acac})_2$). 28 mmol cH , 14 mmol H_2O_2 , 40.0 μmol $\text{Co}(\text{acac})_2$, 30.0 μmol $\text{VO}(\text{acac})_2$, AcOH , 40°C, (1, 3)— $\text{VO}(\text{acac})_2$; (2, 4)— $\text{Co}(\text{acac})_2$.

Nevertheless, detailed investigation of the mechanism of these catalytic systems remains a challenge.

4. CONCLUSIONS

The promoted effect of small additions of glyoxal on the rate of reaction as well as the yield of goal products in catalytic liquid-phase cH oxidation by H_2O_2 has been established. Dialdehyde in such an oxidizing system plays the role of a sacrificial donor producing the additional amount of free-valent species and possibly high-valent metal-oxo species. The high catalytic activity of $\text{VO}(\text{acac})_2$ is attributed to its low redox potential, which facilitated the reduction of hydrogen peroxide by active [catalyst– H_2O_2] intermediate formation resulting in HO^\cdot and putative $\text{V}^{V=O}$ species releasing. This study provides additional experimental data about the fact that hydroxylation reactions of alkanes with hydroperoxides in the presence of d-elements pass in fact by mechanisms involving both free-radical and nonradical pathways [24].

ACKNOWLEDGMENTS

The authors are grateful to Prof. J.-P. Pete for helpful discussion on the research topic. A.P. thanks the NATO Scientific Division for a postdoc fellowship.

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