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Glyoxal-promoted homogeneous catalytic oxygenation of cyclohexane with hydrogen peroxide in the presence of V and Co compounds

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The efficiency of cyclohexane oxidation with hydrogen peroxide catalyzed by vanadyl acetylacetonate at 40 °C and atmospheric pressure is enhanced by glyoxal additive. The process selectively produces a mixture of cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone with a high rate (up to 4400 catalyst turnover number). Cobalt(II) acetylacetonate is much less active but more selective with respect to cyclohexyl hydroperoxide.

Key words: catalysis, oxidation, cyclohexane, vanadyl acetylacetonate, cobalt(II) acetylacetonate, acetic acid, hydrogen peroxide, glyoxal.

The problem of selective and efficient oxidative functionalization of paraffins with the low-cost and environmentally safe oxidative agents, O_2 and H_2O_2, is still drawing attention of researchers.[1—3] The products of cyclohexane (CyH) oxidation, cyclohexanone (CyO), cyclohexanol (CyOH), and cyclohexyl hydroperoxide (CyOOH), are the starting materials for the production of adipic acid and caprolactam that are the monomers for synthetic fibers.[4] Therefore, cyclohexane oxidation is one of the world's largest scale chemical processes.[4] Currently, the industrial oxidation is carried out with air at 160—180 °C and 0.8—1.5 MPa in the presence of a homogeneous cobalt catalyst. The process operates with a conversion of 4—6%, a total selectivity to CyO, CyOH, and CyOOH of 75—80%, and a turnover number of 400—450.[5—7]

Most of the currently proposed methods for cyclohexane oxidation are not competitive with the industrial method yet. In some cases, this is due to the need to operate with very diluted solutions of an alkane under oxidation in order to achieve the high selectivity and conversion.[8] In other cases, for example, when heterogeneous catalysts are used,[9] the technological scheme becomes complicated and therefore extremely expensive.

Recently, an efficient method was developed for alkane oxidation with hydrogen peroxide catalyzed by both heterogeneous[10] and homogeneous[11] vanadium compounds under mild conditions.

In this work, we report on homogeneous cyclohexane oxidation in the presence of soluble vanadyl acetylacetonate $VO(acac)_2$ and acetic acid.

Glyoxal was used as a promoter of CyH oxidation. This non-volatile and untoxic aldehyde was chosen to verify a hypothesis on its possible promoting effect in the reaction under study by analogy with mono-aldehydes.[12] Thus, one could perform CyH oxidation at 40 °C and atmospheric pressure without activators (pyrazine-2-carboxylic acid)[11] with high selectivity (at least 95% based on the converted CyH). The reaction temperature was chosen in such a way as to prevent the CyH escape at elevated temperatures and stratification of the reaction mixture under reduced temperatures.

Experimental

Cyclohexane, acetic acid (both Fluka), $VO(acac)_2$, and $Co(acac)_2$ (both Acros) were used without additional purification. Aqueous solutions of hydrogen peroxide (35%, Aldrich) and glyoxal (30%, Fluka) were concentrated by removing of water on a rotor evaporator to prepare 70% and 45% solutions, respectively.

Cyclohexane oxidation with hydrogen peroxide (general procedure). To a stirred and thermally controlled (40 °C) solution containing CyH (28 mmol), a catalyst (8 μmol), and glyoxal (5 mmol) in AcOH (14 mL) was rapidly added a 70% aqueous solution of H_2O_2 (14 mmol). Then the reaction mixture was

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sampled (1 mL) in specified time intervals and analyzed by GLC and permanganatometry. The total volume of the reaction mixture was 18 mL in all runs.

Concentrations of the unreacted CyH and the oxidation products (CyO, CyOH, and CyOOH) were measured by GLC (chromatograph Hewlett—Packard-5890, series II, flame-ionization detector, capillary column 30 m × 0.25 mm, immobile phase HP-Innowax). To determine CyOOH in the presence of CyO and CyOH, an earlier described procedure was used.[13] In addition to CyO, CyOH, and CyOOH, traces of adipic acid were identified in the oxidation products. The correctness of GLC analysis was verified by a chromatomass-spectrometry (Finnigan Trace MC 2000). Hydrogen peroxide consumption was determined by titration of a part of each sample (0.5 mL) with a 0.01 *N* solution of $KMnO_4$.

Results and Discussion

In preliminary runs, the homogeneous-catalytic oxidation of CyH was performed in the presence of VO(acac)$_2$ ($2.9 \cdot 10^{-4}$ eq) and a 70% solution of H_2O_2 (0.5 eq) in AcOH for 30 min at 40 °C and atmospheric pressure. The formation of a mixture of CyO, CyOH, and CyOOH (1 : 2 : 1 ratio) contradicts the reported data[14] according to which CyOOH was not formed under similar conditions.

Bubbling air or oxygen through an oxidized mixture has a slight effect on the yield of the target products (Table 1, entries *1* and *2*). The CyH conversion somewhat decreases when the reaction is carried out in an argon atmosphere (see Table 1, entry *3*). When a stoichiometric amount of H_2O_2 and a smaller weighed portion of the catalyst (for example, $1.4 \cdot 10^{-4}$ eq) are used, the CyH conversion increases from 3.5 to 5.8%, the relative yield of CyOOH increases, and the CyO yield markedly decreases (see Table 1, entry *4*). A similar ratio of the oxidation products at a conversion of 5.9% is achieved in 3 h in the presence of only $1.8 \cdot 10^{-5}$ eq VO(acac)$_2$ (see Table 1, entry *5*). The preliminary treatment of the catalyst with hydrogen peroxide has no effect on the results of experiments.

In the presence of glyoxal (0.18 eq), the parameters of process are substantially improved. The turnover number

Table 1. Homogeneous-catalytic oxidation of CyH with hydrogen peroxide in acetic acid[a]

Entry	Conditions		Conversion CyH (%)	Consumption H_2O_2 (%)	Selectivity (%)			[CyO + CyOH + CyOOH] /mmol L^{-1}	Catalyst turnover number
	Atmosphere	H_2O_2/mmol			CyO	CyOH	CyOOH		
				VO(acac)$_2$ (8 μmol)					
1	Air	14	3.5	93	27	50	23	54	120
2	O_2 [b]	14	3.6	97	28	52	20	56	125
3	Argon [c]	14	3.1	79	24	45	31	47	105
4 [d]	Air	28	5.8	91	13	45	42	101	455
5 [e]	Air	28	5.9	60	13	41	46	85	3040
				VO(acac)$_2$ (8 μmol) + glyoxal (5 mmol)					
6	Air	14	4.5	97	35	52	13	71	160
7	O_2 [b]	14	4.9	98	34	39	27	76	170
8 [f]	Air	28	7.3	92	33	45	22	113	510
9 [g]	Air	28	7.2	71	16	35	49	122	4400
10 [g]	Argon [c]	28	7.1	73	16	38	46	111	4000
11 [h]	Argon [c]	28	7.2	72	22	40	38	111	2000
12 [i]	Argon [c]	28	6.9	92	34	49	17	108	485
13 [f,i]	Air	28	3.3	92	20	41	39	51	230
				Co(acac)$_2$ (8 μmol)					
14	Air	14	0.5	19	0	1	99	8	17
15	O_2 [b]	14	0.6	18	0	1	99	9	18
				Co(acac)$_2$ (8 μmol) + glyoxal (5 mmol)					
16	Air	14	1.0	43	0	2	98	16	35
17	O_2 [b]	14	1.1	46	0.3	1.7	98	17	36

[a] Reaction conditions: CyH (28 mmol, 1.6 mol L^{-1}), AcOH (14 mL), atmospheric pressure, 40 °C, 30 min.

[b] Oxygen bubbling rate 20 mL min^{-1}.

[c] Argon bubbling rate 30 mL min^{-1}.

[d] $1.4 \cdot 10^{-4}$ eq. VO(acac)$_2$.

[e] $1.8 \cdot 10^{-5}$ eq VO(acac)$_2$.

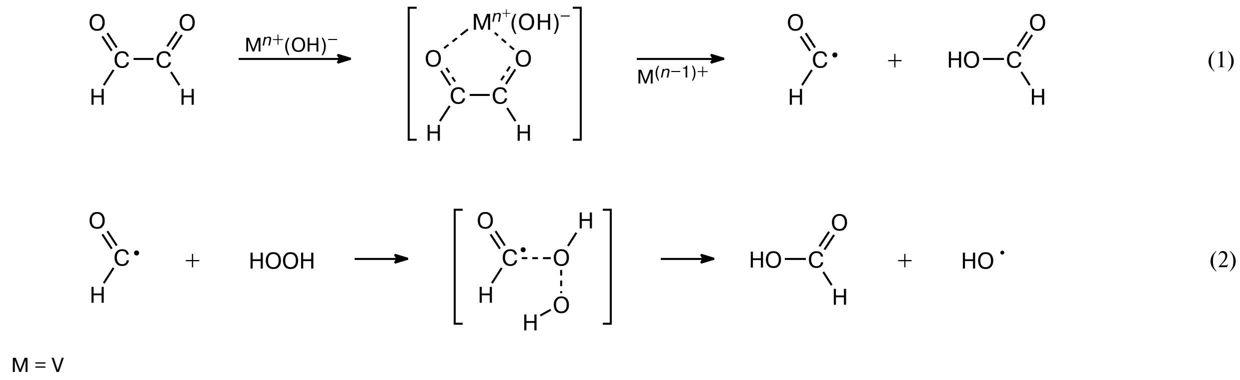
[f] 4 μmol of catalyst.

[g] 0.5 μmol catalyst for reaction time of 180 min.

[h] 1.0 μmol of catalyst.

[i] Isobutyral (20 mmol) was used instead of glyoxal.

Scheme 1



increases by more than 1.4 times (see Table 1, entries *5* and *9*) and the CyH conversion increases by 1.2 times.

A change of glyoxal for isobutyric aldehyde (see Table 1, entry *13*) in the catalytic system under study does not increase the yield of the target products and alkane conversion. The role of glyoxal and mono-aldehyde in this oxidative system is unclear. Meanwhile, one can suggest that the mechanisms of oxidation of these reactants are different and the reactive intermediates are formed in the presence of glyoxal[15] (Scheme 1). The formation of free-radical species by the reaction between glyoxal and vanadium(v) has been reported.[16]

Taking into account that cobalt(ii) naphtenate is the main catalyst for the industrial cyclohexane oxidation,[5—7] we studied the effect of $Co(acac)_2$ on the features of paraffin oxidation in the system under study (see Table 1, entries *14—17*). This catalyst proved to be much less active in CyH oxidation compared to $VO(acac)_2$. The cobalt salt-catalyzed CyH oxidation both in the absence and in the presence of glyoxal afforded CyOOH as the only product. Noteworthy, in the absence of H_2O_2 this catalytic system has no catalytic effect on CyH oxidation irrespectively of the nature of the catalyst used.

It was found on the basis of the kinetic data (Fig. 1) that glyoxal accelerates cyclohexane oxidation and enhances the yield of the target products. In addition, the process catalyzed by $Co(acac)_2$, unlike that catalyzed by the soluble vanadium salt, occurs with a prolonged induction period, which can be reduced by glyoxal additives from 15—20 to 5 min.

Since oxygen bubbling does not significantly affect the yield of the products and the H_2O_2 decomposition rate, one can conclude that the process is controlled mainly by H_2O_2 decomposition to hydroxyl radicals induced by metal cations. The redox potential of the pair V^{IV}/V^{V} ($E^\circ = 1.00$ V) is lower than that of H_2O_2 ($E^\circ = 1.77$ V).[17] As a result, H_2O_2 rapidly oxidizes V^{IV} to V^{V} at pH < 7 with simultaneous formation of highly active hydroxyl radicals, which initiate alkane oxidation. The E° value for the Co^{II}/Co^{III} pair is 0.06 V higher than that for H_2O_2, and due to the difference the generation of the hydroxyl radicals in the catalytic system under study is strongly retarded.

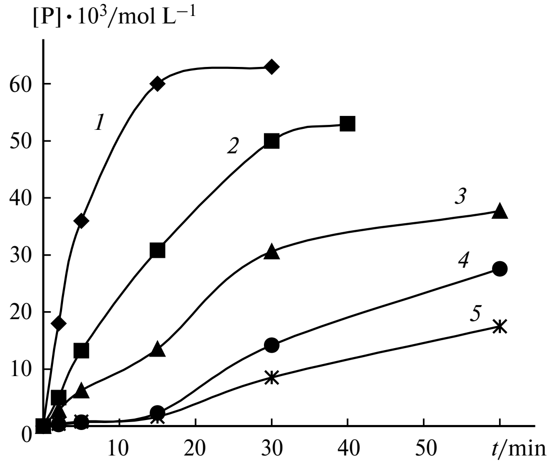


Fig. 1. Kinetics of accumulation of the products of cyclohexane oxidation (P) in air (*1—4*) or argon (*5*) atmosphere in the presence of various catalytic systems: $VO(acac)_2$ + glyoxal (*1*), $VO(acac)_2$ (*2*), $Co(acac)_2$ + glyoxal (*3*), $Co(acac)_2$ (*4*, *5*) (reaction conditions see Table 1).

In experiments with more diluted (35%) hydrogen peroxide, the reaction rate and the yield of the target products markedly decrease (by 1.5—1.8 times). This gives evidence of the essential contribution of the free radicals to the total oxidation rate. In addition, an increase in the water content in the initial reactive mixture results in the layer stratification.

After addition of H_2O_2 green color of the reactive mixture containing $VO(acac)_2$ in AcOH turned to yellow, being accompanied by fast decay of hydrogen peroxide. This change is likely due to the mutual transformations of the reduced (V^{IV}) and oxidized (V^{V}) catalyst species. A change in the poor-pink color (Co^{II}) of the initial reaction solution to green color (Co^{III}) after addition of

H_2O_2 was not observed during oxidation catalyzed by Co(acac)$_2$.

Hence, VO(acac)$_2$ in AcOH in the presence of glyoxal under mild conditions efficiently catalyzes cyclohexane oxidation with hydrogen peroxide to cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide. Addition of dioxygen to the reaction mixture and the use of the cobalt catalyst have virtually no effect on the process under study.

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