

Kinetics and Mechanism of Cyclohexane Oxidation with Molecular Oxygen in the Presence of Propionic Aldehyde

V. I. Timokhin, M. T. Lisovska, and A. P. Pokutsa

Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Lvov, Ukraine

Received September 23, 1998

Abstract—The kinetics and mechanism of the liquid-phase oxidation of cyclohexane with molecular oxygen in the presence of the additives of propionic aldehyde are studied at 303.0, 322.5, and 341.5 K by measuring the rates of oxygen and propionic aldehyde consumption and the yields of the main reaction products (cyclohexanol (COL), cyclohexanone (CON), cyclohexyl hydroperoxide, and propionic acid and peracid). A kinetic scheme is proposed and rate constants of elementary reactions are estimated based on the analysis of their rates and the yields of the main cyclohexane products. The key reactions of the main steps (including chain initiation, propagation, and termination) are determined. An increase in the rate of cyclohexane oxidation and the yield of the target products (cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide) in the presence of propionic aldehyde suggests that highly active acylperoxy radicals participate in chain propagation. The [CON]/[COL] ratio indicates that these products are mainly formed in chain propagation. The strong effect of the Baeyer–Villiger rearrangement on both the rate of oxygen consumption and the yield of the target products at the initial stages of the process and at high propionic aldehyde concentrations is explained.

INTRODUCTION

The liquid-phase oxidation of cyclohexane (CH) with molecular oxygen forms the basis for the industrial production of large-scale intermediate products of organic synthesis (cyclohexanol (COL), cyclohexanone (CON), and adipic acid [1–4]). However, under industrial conditions (cobalt naphthenate; 433–453 K; air pressure, 9–13 torr; and reaction duration, 30 min), the maximum process selectivity is lower than 70% at a cyclohexane conversion of 9% [5]. Therefore, the process occurs at a low rate with a low yield of the target products despite rather severe oxidation conditions.

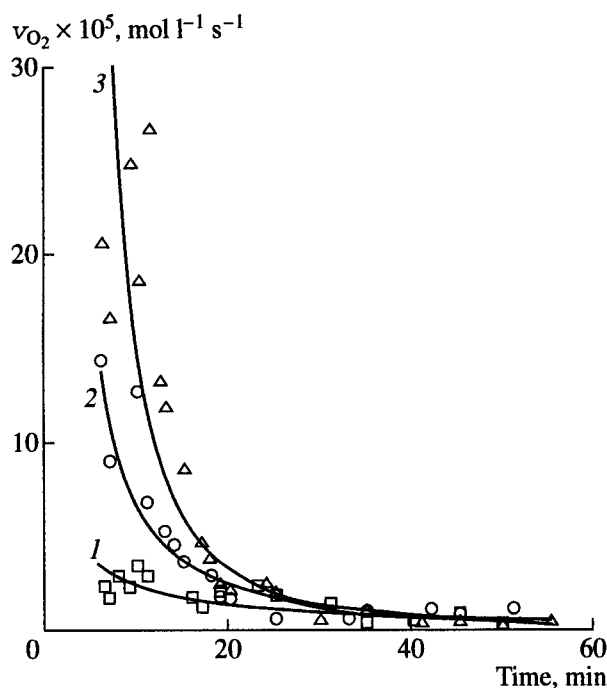
One of the promising methods for intensifying and improving the selectivity of the oxidation of poorly oxidizable compounds (including cyclohexane) is their coupled oxidation with substances that generate ROO· radicals, which are highly active in hydrogen abstraction from the C–H bonds [6, 7]. An increase in the selectivity of this reaction with the peroxy radical activity [7–9] may be used to intensify cyclohexane oxidation. Preliminary studies showed that cyclohexane oxidation with molecular oxygen readily occurs in the presence of not only aldehydes [10, 11], which readily generate *in situ* highly active acylperoxy radicals [6–8, 12, 13], but also organic peracids (for example, μ -chlorobenzoic peracid [14]).

Despite numerous studies devoted to the above problem, the mechanism for the formation of the main products of cyclohexane oxidation with molecular oxygen in the presence of aldehydes remains unclear. Specifically, the mechanisms of the early steps of cyclohexane oxidation with aldehyde and the formation and reactions of the radicals and molecular products have

not been established. The rates of the elementary steps of the process remain unknown. The effect of small aldehyde additives (<0.5 mol/l) at temperatures that are markedly lower than those used in industry (300–350 K) on the yield of the target products of the liquid-phase oxidation of cyclohexane is of particular practical interest.

EXPERIMENTAL

The liquid-phase oxidation of cyclohexane with molecular oxygen in the presence of propionic aldehyde (PA) was conducted on a gasometric setup [15] in glass reactors (oxygen pressure, 0.1 MPa) at 303.0, 322.5, and 341.5 K. The volume of the reaction mixture was 3.0 ml. The reaction vessel was shaken with a frequency that ensured the kinetics control of the process. The oxidation duration was 60 min. The concentration of peroxide compounds in the oxidation products were qualitatively determined by thin-layer chromatography by comparing the retention indices of these products (R_f) with the R_f values for individual peroxides (Silufol plates; eluent, toluene–ethyl acetate mixture (1:1 by volume); developer, saturated acetone solution of NaI). The oxidation products and initial substances were quantitatively analyzed on an LKhM-80 chromatograph equipped with a flame-ionization detector and a steel column (3 m \times 3 mm) packed with Chromaton N-AW covered with a fixed phase of polyphenylmethylsiloxane (5%). Toluene was used as an internal standard. To determine the true cyclohexanol and cyclohexanone concentrations in the presence of cyclohexyl hydroperoxide (CHHP), the mixture was treated with triphenylphosphine. The true cyclohexanol and cyclo-



The rate of oxygen consumption as a function of the duration of cyclohexane oxidation in the presence of (1) 0.05, (2) 0.13, and (3) 0.26 mol/l of propionic aldehyde at 341.5 K.

hexanone concentrations were calculated by the equations derived in [16]. The overall concentrations of cyclohexyl hydroperoxide and propionic peracid (PPAc) were determined by iodometry [17]. The PPAc concentration was determined by subtracting the CHHP concentration (obtained by thin-layer chromatography) from the overall concentration of the peroxide compounds (obtained by iodometry). Cyclohexane was purified as described in [18]. Propionic aldehyde was purified by distillation in a fractionating column in nitrogen.

RESULTS AND DISCUSSION

The representative curves that illustrate how the rate of oxygen consumption (v_{O_2}) changes with the duration of cyclohexane oxidation in the presence of propionic aldehyde at 341.5 K are shown in the figure. The average v_{O_2} value measured within 10 min increases with the propionic aldehyde concentration to 0.26 mol/l (see the figure and Table 1). In the course of oxidation, the rate of oxygen consumption gradually decreases and the reaction virtually ceases in 30–40 min. The curves that illustrate how the rate of oxygen consumption varies with the reaction duration at 303.0 and 322.5 K exhibit the same behavior as those obtained at 341.5 K.

In the absence of propionic aldehyde, cyclohexane is not oxidized at 303.0–341.5 K. Table 1 shows that the propionic aldehyde additives (to 0.5 mol/l) accelerate cyclohexane oxidation and increase both the yield of the target products and the process rate.

Using thin-layer chromatography, we identified three different peroxides in the oxidation products with the R_f values of 0.90, 0.77, and 0.61. The first peroxide is cyclo- $C_6H_{11}OOH$, the second is either α -oxypropylperpropionate $C_2H_5CH(OH)OOC(O)C_2H_5$ or α -hydroxyperoxypropionate $C_2H_5CH(OOH)OC(O)C_2H_5$ [6], and the third is propionic peracid $C_2H_5C(O)OOH$. Traces of cyclohexyl hydroperoxide and propionic peracid in the samples of the oxidation products were identified by comparing their retention indices with the R_f values for individual peroxides. Peroxides with $R_f = 0.77$ may be formed via the Baeyer–Villiger reaction [6] (reactions (22) and (23) in Table 2). The number of peroxides identified in the oxidation products (within the accuracy of the method) depends on both the propionic aldehyde concentration and temperature: three peroxides are identified at high propionic aldehyde concentrations and no peroxide is formed at low propionic aldehyde concentrations. Note that the concentration of the peroxide compound with $R_f = 0.77$ is much lower than that of either propionic peracid or cyclohexyl hydroperoxide. This peroxide compound is only present at high initial concentrations of propionic aldehyde.

Based on the analysis of the composition of the oxidation products and the available data on cyclohexane oxidation with molecular oxygen in the presence of aldehydes, we propose a kinetic scheme for the above process with elementary steps characterized by the parameters given in Table 2.

Table 1 shows that small additives of the propionic aldehyde (≤ 0.48 mol/l) cause an abrupt increase in both the rate of oxygen consumption and the yield of the target products. In this case, the chain initiation in the $CH + PA + O_2$ system occurs via reactions (1)–(3) (Table 2). For example, at $T = 341.5$ K, $[O_2] = 1.0 \times 10^{-2}$ mol/l [44], $[CH]_0 = 9.0$ mol/l, and $[PA]_0 = 0.48$ mol/l, the rates of these reactions v_i (mol l⁻¹ s⁻¹) are

$$\begin{aligned} v_{i,1} &= k_1[PA][O_2] \\ &= (5.7 \times 10^{-4})(0.48)(1.0 \times 10^{-2}) = 2.7 \times 10^{-6}, \\ v_{i,2} &= k_2[PA]^2[O_2] \\ &= (2.0 \times 10^{-6})(0.48^2)(1.0 \times 10^{-2}) = 4.6 \times 10^{-9}, \\ v_{i,3} &= k_3[CH][O_2] \\ &= (2.0 \times 10^{-6})(9.0)(1.0 \times 10^{-2}) = 1.8 \times 10^{-14}. \end{aligned}$$

Here k_1 , k_2 , and k_3 are the rate constants of the corresponding reactions given in Table 2.

Comparison of the $v_{i,1}$, $v_{i,2}$, and $v_{i,3}$ values shows that chain initiation in the system under consideration occurs mainly via reaction (1). This reaction favors an increase in both the rate of oxygen consumption and the yield of the target products of cyclohexane oxidation. Note that the initial chain length $\nu = v_{O_2}/v_i$, which was initially >10 (see the figure), decreases to unity during the first 10 min of the reaction. The low rate of reaction (3) ($\sim 10^{-14}$ mol l⁻¹ s⁻¹) indicates that chain initiation in

Table 1. Effect of the initial propionic aldehyde concentration and temperature on both the rate of oxygen consumption and the yield of the products of cyclohexane and propionic aldehyde oxidation ($[\text{CH}]_0 = 9.1 \text{ mol/l}$; overall reaction duration, 60 min)

[PA] ₀ , mol/l	ν _{O₂} × 10 ⁵ , mol l ⁻¹ s ⁻¹	[COL]	[CON]	[CHHP]	ΣP*	[CON]/[COL]	[PPAc] × 10 ² , mol/l	[PA]**, mol/l	[PA] + [PPAc]	[PAc]***
		×10 ³ , mol/l							mol/l	
303.0 K										
0.13	0.50	0.2	0.2	0	0.4	1.0	0.2	—	—	—
0.26	0.91	1.5	1.4	3.1	6.0	1.1	3.0	0.13	0.16	0.10
0.48	—	2.2	—	—	—	—	0.6	0.27	0.28	0.20
322.5 K										
0.05	0.32	Traces	Traces	0	Traces	—	0.2	—	—	—
0.13	3.75	10.9	7.7	3.0	21.6	1.4	5.2	0.10	0.15	0
0.26	>12.9	21.2	19.4	10.2	50.8	1.1	4.3	0.03	0.07	0.19
341.5 K										
0.05	2.28	18.4	15.0	0.	33.4	1.2	1.8	0.02	0.04	0.01
0.13	12.0	30.2	25.5	1.0	56.7	1.2	2.0	0.11	0.13	0
0.26	20.2	39.5	26.7	0.6	66.7	1.5	3.1	0.15	0.18	0.08
0.48	3.07	32.9	20.9	6.6	60.4	1.6	4.6	0.27	0.32	0.16

* $\Sigma \text{P} = [\text{COL}] + [\text{CON}] + [\text{CHHP}]$.

** Residual concentration of propionic aldehyde.

*** $[\text{PAC}] = [\text{PA}]_0 - ([\text{PA}] + [\text{PPAc}])$.

the course of the reaction of cyclohexane with molecular oxygen does not occur.

The $\text{RC}^{\cdot}(\text{O})$ acyl radicals formed via reaction (1) may be consumed via reactions (4) and (6), the rates of which at 341.5 K are

$$v_4 = k_4[\text{RC}^{\cdot}(\text{O})][\text{O}_2] = 1.2 \times 10^9[\text{RC}^{\cdot}(\text{O})] \times 1.0 \times 10^{-2} \\ = 1.2 \times 10^7[\text{RC}^{\cdot}(\text{O})] \text{ mol l}^{-1} \text{ s}^{-1},$$

$$v_6 = k_6[\text{RC}^{\cdot}(\text{O})] = 8.9 \times 10^5[\text{RC}^{\cdot}(\text{O})] \text{ s}^{-1}.$$

The value of $v_4/v_6 = 13.5$ indicates that more than 90% of the $\text{RC}^{\cdot}(\text{O})$ radicals transform into acylperoxy $\text{RC}(\text{O})\text{OO}^{\cdot}$ radicals. Therefore, the decarbonylation of acyl radicals (reaction (4)) is of minor importance in the process under consideration. The resulting acylperoxy radicals are consumed via two competitive reactions (8) and (9), the rates of which at $T = 341.5 \text{ K}$, $[\text{CH}]_0 = 9.0 \text{ mol/l}$, $[\text{PA}]_0 = 0.48 \text{ mol/l}$ are

$$v_8 = k_8[\text{RC}(\text{O})\text{OO}^{\cdot}][\text{CH}] \\ = 1.4 \times 10^3[\text{RC}(\text{O})\text{OO}^{\cdot}] \times 9.0 \\ = 1.3 \times 10^4[\text{RC}(\text{O})\text{OO}^{\cdot}] \text{ mol l}^{-1} \text{ s}^{-1}, \\ v_9 = k_9[\text{RC}(\text{O})\text{OO}^{\cdot}][\text{PA}] \\ = 5.4 \times 10^4[\text{RC}(\text{O})\text{OO}^{\cdot}] \times 0.48 \\ = 2.6 \times 10^4[\text{RC}(\text{O})\text{OO}^{\cdot}] \text{ mol l}^{-1} \text{ s}^{-1}.$$

The v_8/v_9 ratio is 0.5. Therefore, the $\text{RC}(\text{O})\text{OO}^{\cdot}$ radicals transform into propionic peracid via both reac-

tions. Note that the v_8/v_9 ratio increases and becomes much higher than 0.5 as the initial concentration of propionic aldehyde decreases and the oxidation conversion increases. This favors an increase in the relative fraction of cyclohexane involved in the oxidation. The data in Table 1 show that the most reasonable propionic aldehyde concentration is $\leq 0.26 \text{ mol/l}$ (at 341.5 K). Otherwise, at $[\text{PA}] > 0.26 \text{ mol/l}$, most of the $\text{RC}(\text{O})\text{OO}^{\cdot}$ radicals react with aldehyde to give propionic peracid, which decreases the yield of the target products. At the same time, the use of very low initial concentrations of propionic aldehyde ($\leq 0.26 \text{ mol/l}$) is also unreasonable because it favors a dramatic decrease in both the process rate and the yield of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide. The best method for the identification of cyclohexane oxidation is the periodic introduction of small additives of propionic aldehyde into the system. In this case, the process rate is somewhat lower, but the yield of the target products is higher.

The cyclohexyl radicals formed via reaction (8) transform into the cyclohexylperoxy radicals and this transformation is diffusion-controlled. The cyclohexylperoxy radicals participate in two reactions, (11) and (12), the rates of which at $T = 341.5 \text{ K}$, $[\text{CH}]_0 = 9.0 \text{ mol/l}$, $[\text{PA}]_0 = 0.48 \text{ mol/l}$ are

$$v_{11} = k_{11}[\text{cyclo-C}_6\text{H}_{11}\text{OO}^{\cdot}][\text{CH}] \\ = 0.2[\text{cyclo-C}_6\text{H}_{11}\text{OO}^{\cdot}] \times 9.0 \\ = 1.8[\text{cyclo-C}_6\text{H}_{11}\text{OO}^{\cdot}] \text{ mol l}^{-1} \text{ s}^{-1},$$

Table 2. Kinetic scheme and elementary steps of cyclohexane oxidation with molecular oxygen in the presence of propionic aldehyde

Reaction no.	Reaction	Preexponential factor ^a	Activation energy, kJ/mol	k_i^a	Reference
1	$\text{RCHO} + \text{O}_2 \longrightarrow \text{RC}'(\text{O}) + \text{HOO}'$ ($\text{R} = \text{C}_2\text{H}_5$)	4.5×10^{14}	117.0	3.0×10^{-6} (303 K) 5.7×10^{-4} (341.5 K)	[19]
2	$2\text{RCHO} + \text{O}_2 \longrightarrow 2\text{RC}'(\text{O}) + \text{H}_2\text{O}_2$ ($\text{R} = \text{C}_3\text{H}_7$)	2.0×10^3	59.0	1.3×10^{-1} (303 K) 2.0×10^{-6} (341.5 K)	[19]
3	$\text{cyclo-C}_6\text{H}_{12} + \text{O}_2 \longrightarrow \text{cyclo-C}_6\text{H}_{11} + \text{HOO}'$	7.9×10^{12}	167.4	1.1×10^{-16} (303 K) 2.0×10^{-13} (341.5 K)	[20]
4	$\text{RC}'(\text{O}) + \text{O}_2 \longrightarrow \text{RC}(\text{O})\text{OO}'$	—	—	1.2×10^9 (303 K) 1.2×10^9 (341.5 K)	[21]
5	$\text{cyclo-C}_6\text{H}_{11} + \text{O}_2 \longrightarrow \text{cyclo-C}_6\text{H}_{11}\text{OO}'$	—	—	2.0×10^9 (303 K) 2.0×10^9 (341.5 K)	[22]
6	$\text{RC}'(\text{O}) \longrightarrow \text{R}' + \text{CO}$ ($\text{R} = (\text{CH}_3)_3\text{C}$)	7.9×10^{11}	38.9	1.6×10^5 (303 K) 8.9×10^5 (341.5 K)	[23]
7	$\text{HOO}' + \text{RCHO} \longrightarrow \text{RC}'(\text{O}) + \text{H}_2\text{O}_2$ ($\text{R} = \text{C}_2\text{H}_5$)	3.1×10^8	37.5	1.0×10^2 (303 K) 5.7×10^2 (341.5 K)	[24]
8	$\text{RC}(\text{O})\text{OO}' + \text{cyclo-C}_6\text{H}_{12} \longrightarrow \text{RC}(\text{O})\text{OOH} + \text{cyclo-C}_6\text{H}_{11}$ ($\text{R} = \text{Ph}$)	7.6×10^{13}	70.2	60^b (303 K) 1.4×10^3 (341.5 K)	Our estimates
9	$\text{RC}(\text{O})\text{OO}' + \text{RCHO} \longrightarrow \text{RC}(\text{O})\text{OOH} + \text{RC}'(\text{O})$ ($\text{R} = \text{C}_2\text{H}_5$)	4.2×10^9	32.0	1.3×10^4 (303 K) 5.4×10^4 (341.5 K)	[28]
10	$\text{HOO}' + \text{cyclo-C}_6\text{H}_{12} \longrightarrow \text{H}_2\text{O}_2 + \text{cyclo-C}_6\text{H}_{11}$ ($\text{R} = \text{C}_2\text{H}_5$)	—	—	0.46^c (303 K) 14.8 (341.5 K)	Our estimates
11	$\text{cyclo-C}_6\text{H}_{11}\text{OO}' + \text{cyclo-C}_6\text{H}_{12} \longrightarrow \text{cyclo-C}_6\text{H}_{11}\text{OOH} + \text{cyclo-C}_6\text{H}_{11}$	1.6×10^8	57.7	1.8×10^{-2} (303 K) 0.2 (341.5 K)	[29]
12	$\text{cyclo-C}_6\text{H}_{11}\text{OO}' + \text{RCHO} \longrightarrow \text{cyclo-C}_6\text{H}_{11}\text{OOH} + \text{RC}'(\text{O})$	—	—	3.9^d (303 K) 7.7 (341.5 K)	Our estimates
13	$\text{RC}(\text{O})\text{OOH} \longrightarrow \text{RC}(\text{O})\text{O}' + \text{HO}'$ ($\text{R} = \text{CH}_3$)	1.4×10^8	84.1	4.4×10^{-7} (303 K) 1.9×10^{-5} (341.5 K)	[30]
14	$\text{RC}(\text{O})\text{O}' \longrightarrow \text{R}' + \text{CO}_2$ ($\text{R} = \text{C}_2\text{H}_5$)	—	—	3.3×10^{10} (343 K) $\sim 3.3 \times 10^{10}$ (341.5 K)	[31]
15	$\text{RC}(\text{O})\text{O}' + \text{cyclo-C}_6\text{H}_{12} \longrightarrow \text{RC}(\text{O})\text{OH} + \text{cyclo-C}_6\text{H}_{11}$ ($\text{R} = \text{Ph}$)	4.3×10^8	16.3	6.7×10^5 (303 K) 1.9×10^{-6} (341.5 K)	[32]
16	$\text{RC}(\text{O})\text{O}' + \text{RCHO} \longrightarrow \text{RC}(\text{O})\text{OH} + \text{RC}'(\text{O})$	9.8×10^8	15.2	2.3×10^{6e} (343 K) 4.6×10^6 (341.5 K)	Our estimates
17	$\text{cyclo-C}_6\text{H}_{11}\text{OOH} \longrightarrow \text{cyclo-C}_6\text{H}_{11}\text{O}' + \text{HO}'$	1.2×10^{13}	142.3	3.5×10^{-12} (303 K) 2.1×10^{-9} (341.5 K)	[33]
18	$\text{cyclo-C}_6\text{H}_{11}\text{O}' + \text{RCHO} \longrightarrow \text{cyclo-C}_6\text{H}_{11}\text{OH} + \text{RC}'(\text{O})$	9.8×10^8	15.2	2.3×10^{6e} (303 K) 4.6×10^6 (341.5 K)	Our estimates

Table 2. (Contd.)

Reaction no.	Reaction	Preexponential factor ^a	Activation energy, kJ/mol	k_i^a	Reference
19	cyclo-C ₆ H ₁₁ O [•] + cyclo-C ₆ H ₁₂ → cyclo-C ₆ H ₁₁ OH + cyclo-C ₆ H ₁₁ [•]	1.8×10^8	13.4	8.8×10^5 (303 K) 1.6×10^6 (341.5 K)	[34]
20	HO [•] + RCHO → H ₂ O + RC(O) [•] (R = CH ₃)	5.2×10^{10}	10.0	9.8×10^8 (303 K) 1.5×10^9 (341.5 K)	[35]
21	HO [•] + cyclo-C ₆ H ₁₂ → H ₂ O + cyclo-C ₆ H ₁₁ [•] (R = C ₂ H ₅)	1.6×10^{10}	3.2	4.6×10^9 (303 K) 5.2×10^9 (341.5 K)	[36]
22	RC(O)OOH + RCHO → RCH(OH)OOC(O)R (R = CH ₃)	2.2×10^3	23.0	0.24 (303 K) 0.67 (341.5 K)	[37]
23	RCH(OH)OOC(O)R → 2RC(O)OH (R = CH ₃)	9.5×10^9	79.5	1.9×10^{-4f} (303 K) 6.6×10^{-3} (341.5 K)	Our estimates
24	2HOO [•] → O ₂ + H ₂ O ₂	—	—	1.3×10^9 (303 K) 1.3×10^9 (341.5 K)	[39]
25	2cyclo-C ₆ H ₁₂ OO [•] → O ₂ + cyclo-C ₆ H ₁₁ OH + cyclo-C ₆ H ₁₀ O	2.0×10^9	5.4	2.3×10^6 (303 K) 3.0×10^6 (341.5 K)	[40]
26	2RC(O)OO [•] → O ₂ + RC(O)OOC(O)R (R = C ₂ H ₅)			1.0×10^8 (273 K) 1.0×10^8 (341.5 K)	41
27	cyclo-C ₆ H ₁₁ OO [•] + HOO [•] → cyclo-C ₆ H ₁₁ OOH + O ₂	1.2×10^8	0	1.2×10^8 (249–298 K) 1.2×10^8 (341.5 K)	42
28	cyclo-C ₆ H ₁₁ OO [•] + RC(O)OO [•] → O ₂ + RC(O)OH + cyclo-C ₆ H ₁₀ O			3.0×10^{7g} (303 K) 3.4×10^7 (341.5 K)	Our estimates
29	HOO [•] + RC(O)OO [•] → O ₂ + RC(O)OOH (R = CH ₃)	7.8×10^9	–8.6	7.8×10^9 (303 K) 1.6×10^{11} (341.5 K)	43

^a Expressed in s^{–1}, l mol^{–1} s^{–1}, and l² mol^{–2} s^{–1} for the first-, second- and third-order reactions, respectively.

^b The C₂Cl₅OO[•] and PhC(O)OO[•] radicals exhibit the same reactivity in the reaction with cyclohexane ($k_8 = 2.2 \times 10^3$ l mol^{–1} s^{–1} at 348 K) [25]. The activation energy for this reaction was calculated by the equation $E_8 = 0.55D(\text{cyclo-C}_6\text{H}_{11}\text{–H}) = 146.6$ kJ/mol [26], where $D(\text{cyclo-C}_6\text{H}_{11}\text{–H})$ is the C–H bond strength in cyclohexane equal to 399.6 kJ/mol [27].

^c Using the kinetic parameters for reactions (7)–(9), the rate constant for the reaction of the HOO[•] radical with cyclohexane was calculated by the equation $k_{10} = k_8 k_7 / k_9$.

^d Using the kinetic parameters for reactions (8), (9), and (11), the rate constant for the reaction of the cyclo-C₆H₁₁OO[•] radical with RC(O)H was calculated by the equation $k_{12} = k_9 k_{11} / k_8$.

^e The rate constant for this reaction at 399 K was set equal to 1.0×10^7 l mol^{–1} s^{–1} and its activation energy was taken equal to 15.2 kJ/mol, as for the reaction of the (CH₃)₃CO[•] radical with CH₃C(O)H [12].

^f The rate constant for this reaction at 298 K was set equal to 1.1×10^{-4} s^{–1} [38], and its activation energy was taken equal to 79.5 kJ/mol [37].

^g The rate constant for reaction (28) at 341.5 K was assumed to be $k_{28} = 2(k_{25}k_{12})^{1/2}$ l.

$$\begin{aligned}
 v_{12} &= k_{12}[\text{cyclo-C}_6\text{H}_{11}\text{OO}^{\bullet}][\text{PA}] \\
 &= 7.7[\text{cyclo-C}_6\text{H}_{11}\text{OO}^{\bullet}] \times 0.48 \\
 &= 3.7[\text{cyclo-C}_6\text{H}_{11}\text{OO}^{\bullet}] \text{ mol l}^{-1} \text{ s}^{-1}.
 \end{aligned}$$

The fact that $v_{11}/v_{12} = 0.5$ suggests that cyclohexyl hydroperoxide is formed via two competitive reactions (11) and (12). The v_{11}/v_{12} value becomes much higher than 0.5 as the initial concentration of propionic aldehyde decreases and the oxidation duration increases, which causes a decrease in the cyclohexyl hydroperoxide yield in the reaction of the C₆H₁₁OO[•] radicals with propionic aldehyde.

Note that the yield of propionic peracid is low compared to the consumption of propionic aldehyde (Table 1), especially at high initial concentrations of the latter. Obviously, propionic peracid, formed via reac-

tions (8) and (9), may be consumed via reactions (13) and (22) that occur at the rates

$$v_{13} = k_{13}[\text{PPAc}] = 1.9[\text{PPAc}] \text{ s}^{-1},$$

$$v_{22} = k_{22}[\text{PPAc}][\text{PA}] = 0.67[\text{PPAc}][\text{PA}] \text{ mol l}^{-1} \text{ s}^{-1}.$$

Assuming that 50% of propionic aldehyde transforms into propionic peracid, the rates of these two reactions at $T = 341.5 \text{ K}$ and $[\text{PA}]_0 = 0.48 \text{ mol/l}$ are

$$v_{13} = (1.9 \times 10^{-5})(0.24) = 4.6 \times 10^{-6} \text{ s}^{-1},$$

$$v_{22} = (0.67)(0.24)(0.24) = 3.9 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}.$$

Then $v_{22}/v_{13} = 8.5 \times 10^3$, and this indicates the rapid consumption of propionic peracid via the Baeyer–Villiger reaction [37, 45], resulting in the formation of intermediate α -oxypropyl perpropionate or α -hydroxyperoxypropionate. Finally, these peroxide compounds decompose via reaction (23) (Table 2) to give propionic acid. Because the rate of the thermal decomposition of propionic peracid via reaction (13) is much lower than that of the Baeyer–Villiger rearrangement (reactions (22) and (23)), the contributions of both decarboxylation (reaction (14)) and chain propagation (reactions (15) and (16)) to the overall process rate are insignificant.

Cyclohexyl hydroperoxide formed during cyclohexane oxidation cannot efficiently initiate the process under the given conditions because of the low rate of its thermal decomposition (reaction (17)). Indeed, at $T = 341.5 \text{ K}$ and $[\text{CHHP}] = 0.1 \text{ mol/l}$, this rate is

$$v_{17} = k_{17}[\text{CHHP}]$$

$$= (2.1 \times 10^{-9})(0.1) = 2.1 \times 10^{-10} \text{ mol l}^{-1} \text{ s}^{-1},$$

which is markedly lower than the rate of reaction (1).

Table 1 shows that, at $T = 303.0 \text{ K}$ and $[\text{PA}]_0 = 0.26 \text{ mol/l}$, the overall yield of cyclohexanol and cyclohexanone is approximately equal to the yield of cyclohexyl hydroperoxide. At the same time, the $([\text{COL}] + [\text{CON}])$ value is higher than the $[\text{CHHP}]$ at 322.5 and 341.5 K. Moreover, the average value of $[\text{CON}]/[\text{COL}]$ is approximately equal to 1.3 at these temperatures. Therefore, the greatest part of both cyclohexanol and cyclohexanone are formed during chain termination (reactions (25) and (28)).

Thus, our findings suggest that the rate of the chain liquid-phase oxidation of cyclohexane with molecular oxygen in the presence of propionic aldehyde at $[\text{PA}]_0 \leq 0.48 \text{ mol/l}$ and $T = 300\text{--}350 \text{ K}$ is largely determined by the rates of chain initiation (reaction (1)), propagation (reactions (8), (9), (11), and (12)), termination (reactions (25) and (28)), and the Baeyer–Villiger rearrangement (reactions (22) and (23)). An increase in both the rate of cyclohexane oxidation and the yield of the target products (cyclohexanol and cyclohexanone) is due to the participation of highly reactive acylperoxy radicals in chain propagation. Note that, at early stages of the reaction, when the chain length $v > 10$, the rates of the oxidation of propionic aldehyde and cyclohexane

are comparable. In the course of the process ($\tau > 10 \text{ min}$), when the concentration of propionic aldehyde $[\text{PA}]$ becomes much lower than its initial concentration $[\text{PA}]_0$ and the chain length $v \approx 1$, cyclohexane is more intensively oxidized via two main competitive reactions of chain propagation (8) and (9). The contributions of the reactions of the thermal decomposition of cyclohexyl hydroperoxide and propionic peracid, decarboxylation of the RC(O)O^\bullet radicals, and the reactions involving cyclo- $\text{C}_6\text{H}_{11}\text{O}^\bullet$, HO^\bullet , and RC(O)O^\bullet radicals to the overall process rate are insignificant.

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