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# Effect of Quinones on the Cobalt(II) Acetate–Catalyzed Mild Oxidation of Cyclohexane with Hydrogen Peroxide in Acetic Acid

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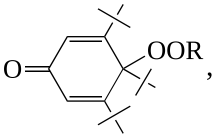
**Abstract**—The effects of free-radical reaction inhibitors (InH), hydroquinone (HQ) and quinone (Q), on the oxidation of cyclohexane catalyzed by cobalt(II) acetate $Co(OAc)_2 \cdot 4H_2O$ and on the decomposition of hydrogen peroxide in acetic acid (HOAc) at 303 K were studied. It was found that an increase in the concentration of HQ in the starting reaction mixture containing cyclohexane, the catalyst, and $H_2O_2$ dissolved in HOAc resulted in an exponential decrease in the yields of the target products of oxidation: cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide. In the presence of Q, the dependence of the yield of the target products on the initial inhibitor concentration exhibited a maximum at $(1.8–2.5) \times 10^{-2}$ M Q. At $(2.2–2.4) \times 10^{-2}$ M Q concentrations, the yield of the target products was 55–60% of that in an uninhibited process. Based on kinetic, spectrometric, and quantum-chemical data, the effect found was explained by the fact that under the experimental conditions highly active hydroxyl derivatives of radicals rather than a hydroxy quinolide hydroperoxide (the homolysis of which can produce species with a free valence, which are capable of initiating free-radical reactions) were largely formed from Q.

## INTRODUCTION

Current processes for the homogeneous oxidation and stabilization of hydrocarbons (reagents for petrochemical synthesis, fuels, and solvents) require the use of low-waste, energy-saving, and environmentally sound technologies. These technologies cannot be created without the development of new highly efficient catalytic processes and fundamental studies of the relevant reaction mechanisms. Therefore, the catalytic liquid-phase oxidation of cyclohexane as a model reaction, which is of interest from both the technological and fundamental points of view, has been the focus of attention for many researchers [1–5]. The effects of various factors (the nature of the catalyst cation (Fe, Co, Ni, V, and Mn) [6–9], the solvent [7–9], and the oxidizing agent [7–11]) on the yield, selectivity, and reaction mechanism were studied. Based on the cited data, we can conclude that, as a rule, the tested catalytic systems are of theoretical interest because the cyclohexane content of the oxidized mixture was insignificant (1–10%) and expensive solvents (pyridine, acetonitrile, and dichloromethane) and oxidants ($KHSO_5$, NaClO, PhIO, and alkyl peroxides) were used.

On the other hand, in our opinion, the mechanisms of catalytic reactions that occur in the course of cyclohexane oxidation by bound oxygen in solvents could be studied better with the use of the inhibitor method, which is widely used in kinetic experiments.

According to published data (see [12] and references therein), the mechanisms of action of inhibitors from different classes on the oxidation of hydrocarbons are known in considerable detail. However, in our opinion, it was reasonable to study the effects of nonphenolic inhibitors (InH) (quinone (Q) and hydroquinone (HQ)) on the cobalt(II) acetate–catalyzed oxidation of cyclohexane by free ($O_2$) and bound ($H_2O_2$) oxygen in an inexpensive solvent (acetic acid (HOAc)). It is well known [13] that alkylphenols, which are commonly used as inhibitors of free-radical reactions, can form quinolide peroxides  , which can subsequently initiate the oxidation of organic compounds [14]. Therefore, it was of interest to check whether compounds of this type can be formed in the case of using inhibitors from the quinone series and to examine the mechanism of action of these inhibitors in the promising cyclohexane–$H_2O_2$–$Co(OAc)_2$–HOAc catalytic system. Hydrogen peroxide was chosen as a promoter oxidant because it is relatively inexpensive, easy to use [15], and readily soluble in HOAc; note that the given oxidation system is scantily known.

## EXPERIMENTAL

The kinetics of product buildup in the course of cyclohexane oxidation in an HOAc solution containing dissolved $H_2O_2$ and $Co(OAc)_2$ was studied in a thermostated 25-ml glass cell equipped with a bubbler for blowing $O_2$ and with a Teflon magnetic stirrer for homogenizing the reaction medium. All the experiments were performed at 303 ± 0.1 K in order to prevent losses of volatile reactants, primarily, cyclohexane. The total volume of the reaction mixture was 10 ml. The stirring was stopped after 7 h of oxidation, and the oxidation products were sampled for thin-layer chromatography (TLC), gas–liquid chromatography, and chemical analysis.

The qualitative analysis of peroxide compounds was performed using TLC by comparing the retention factors ($R_f$) of compounds to the $R_f$ values for individual peroxides (Silufol plates, a toluene and ethyl acetate mixture in a ratio of 1 : 1 as an eluant, and a saturated NaI solution in acetone as a visualizing reagent). The quantitative determination of the initial reactants was performed on an LKhM-80 chromatograph (FID; a 4 m × 3 mm steel column packed with Silicone OV-351 (5%) on Chromaton N-AW). Toluene was used as an internal standard. To determine the true concentrations of cyclohexanol and cyclohexanone in the presence of cyclohexyl hydroperoxide, the samples of oxidation products were treated with triphenylphosphine. The previously published procedure [16] was used in the calculations. The concentration of unreacted $H_2O_2$ was found as the difference between the total concentration of peroxide compounds determined by manganometry and the cyclohexyl hydroperoxide concentration determined by gas chromatography.

Spectrometric measurements were performed on an SF-20 double-beam spectrophotometer with the use of quartz cells (with a width of 1 cm).

Cyclohexane and HOAc were purified in accordance with published procedures [17]. Hydrogen peroxide (30%) and $Co(OAc)_2 \cdot 4H_2O$ (Fluka) were used in the experiments without additional purification.

Commercial hydroquinone was purified by sublimation. Quinone was synthesized according to the published procedure [18] and purified by double recrystallization from ethanol.

## RESULTS AND DISCUSSION

The main results obtained in the study of the cyclohexane–$H_2O_2(O_2)$–$Co(OAc)_2$–HOAc catalytic system were published in [19]. This work is a continuation of this study. Tables 1 and 2 and Fig. 1 summarize the experimental data obtained in the study of the effects of HQ and Q on the mild oxidation of cyclohexane and on the composition of products in the above catalytic system and the interpretation of these data. As follows from Fig. 1, the shapes of the buildup curves of target products on varying the initial concentrations of InH in the reaction mixture depend on the nature of the inhibitor. In the presence of HQ, the total yield of target products decreased with the concentration of InH in accordance with an exponential law; this fact suggests that the reaction of cyclohexane oxidation in the test system occurs completely (or almost completely) via a free-radical mechanism. The contribution of nonradical (or ion–radical) steps to the overall mechanistic scheme of the oxidation should also not be ignored based on a high initial InH concentration of (0.6–0.8) × $10^{-2}$ M, which should be produced in the reaction mixture for halving the total yield of target products, as compared with an uninhibited process (over the same time interval) (Fig. 1). In the case of the occurrence of the oxidation reaction via only a free-radical mechanism, the above concentration of InH did not exceed (0.1–0.2) × $10^{-2}$ M [3]. Similar dependence of the total yield of target products on the concentration of InH was also

**Table 1.** Composition of cyclohexane oxidation products and the consumption of $H_2O_2$ depending on the initial concentration of hydroquinone (HQ) in the oxidized mixture

| $[HQ] \times 10^2$, M | $[Product] \times 10^2$, M | | | Consumption of $H_2O_2$, % |
|---|---|---|---|---|
| | [Cyclohexanol] | [Cyclohexanone] | [Cyclohexyl hydroperoxide] | |
| 0 | 1.50 | 4.6 | 5.0 | 81 |
| 0* | 0.0 | 0.0 | 0.0 | 35 |
| 0.27 | 0.10 | 1.50 | 6.0 | 88 |
| 0.45 | 0.40 | 2.10 | 5.50 | 87 |
| 0.90 | 0.05 | 1.50 | 3.30 | 86 |
| 1.35 | 0.05 | 0.30 | 1.30 | 74 |
| 1.80 | 0.20 | 0.50 | 0.6 | 63 |
| 2.25 | 0.01 | 0.03 | 0.05 | 77 |
| 2.70 | traces | 0.10 | 0.1 | 79 |

Note: $[Cyclohexane]_0$ = 4.2 M; $[Co(OAc)_2]_0$ = 2.0 × $10^{-3}$ M; $[H_2O_2]_0$ = 1.0 M; $v(O_2)$ = 1.0 ml/min; 303 K; 1.0 atm.
* In the absence of $Co(OAc)_2 \cdot 4H_2O$.

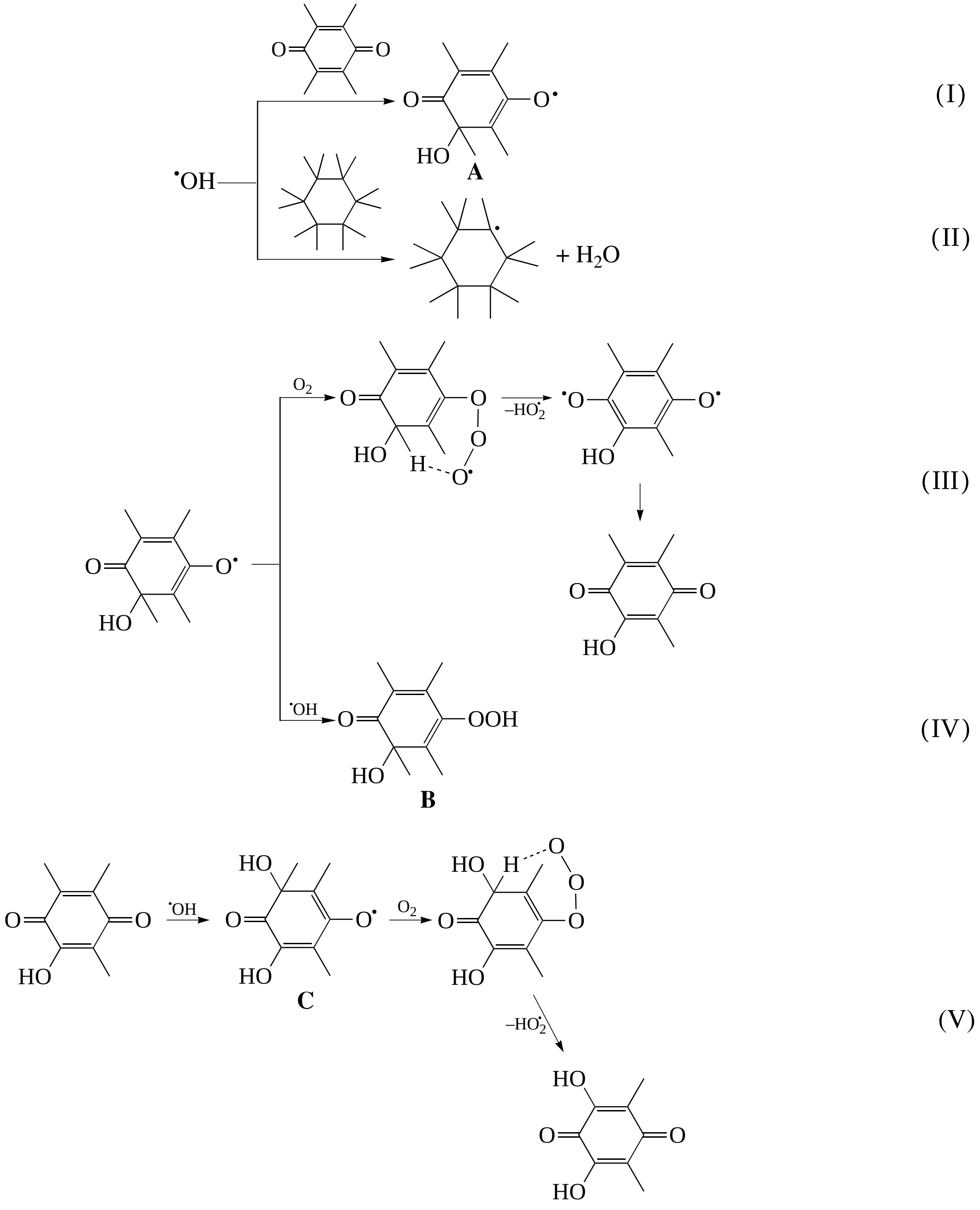
**Table 2.** Composition of cyclohexane oxidation products and the consumption of $H_2O_2$ depending on the initial concentration of quinone (Q) in the oxidized mixture

| $[Q] \times 10^2$, M | $[Product] \times 10^2$, M | | | Consumption of $H_2O_2$, % |
|---|---|---|---|---|
| | [Cyclohexanol] | [Cyclohexanone] | [Cyclohexyl hydroperoxide] | |
| 0.23 | 0.5 | 2.6 | 4.5 | 83 |
| 0.46 | 0.4 | 1.8 | 6.0 | 74 |
| 0.92 | 0.2 | 1.1 | 2.3 | 62 |
| 1.15 | 0.35 | 1.45 | 1.7 | 72 |
| 1.38 | traces | traces | traces | 90 |
| 1.61 | 0.2 | 1.3 | 1.8 | 78 |
| 1.84 | 0.2 | 0.7 | 0.4 | 88 |
| 2.30 | 0.9 | 2.3 | 3.5 | 79 |
| 2.76 | 0.05 | 0.25 | 0.2 | 68 |
| 3.22 | 0.5 | 0.9 | 0.2 | 79 |

Note: $[Cyclohexane]_0$ = 4.2 M; $[Co(OAc)_2]_0$ = 2.0 × $10^{-3}$ M; $[H_2O_2]_0$ = 1.0 M; $v(O_2)$ = 1.0 ml/min; 303 K; 1.0 atm.

observed with Q up to a concentration of (1.3–1.6) × $10^{-2}$ M. However, starting from a Q concentration of (1.6–1.8) × $10^{-2}$ M, the yield of target products increased proportionally to the concentration of quinone and reached a maximum at (2.2–2.4) × $10^{-2}$ M. A further increase in the inhibitor content of the initial reaction mixture inhibited the oxidation, and the buildup of target products was almost terminated at a concentration of ≥3.0 × $10^{-2}$ M. This unusual behavior (passing through a maximum) of the dependence of the buildup of cyclohexane oxidation products on the concentration of InH can be explained by the dual (inhibiting and accelerating) function of quinone.

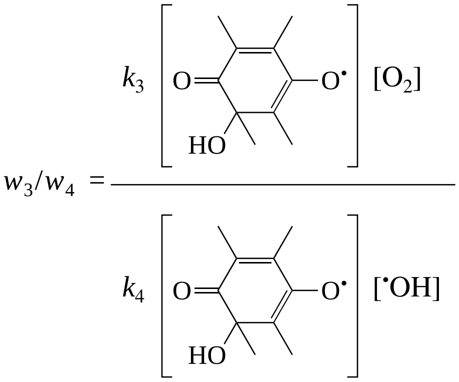
We assume that, under the test process conditions, unstable hydroxy quinolide peroxides and active intermediates with a free valence can be formed from Q, by analogy with alkylphenols, in the following competitive reactions of the hydroxy radical with substrates, including InH, present in the reaction mixture (Scheme 1):



$k_1 = 10^9$ l mol$^{-1}$ s$^{-1}$, $k_2 = 10^8$ l mol$^{-1}$ s$^{-1}$, $k_3 = (10^8–10^9)$ l mol$^{-1}$ s$^{-1}$, $k_4 = 10^9$ l mol$^{-1}$ s$^{-1}$, $k_5 = 10^9$ l mol$^{-1}$ s$^{-1}$ [3, 20].

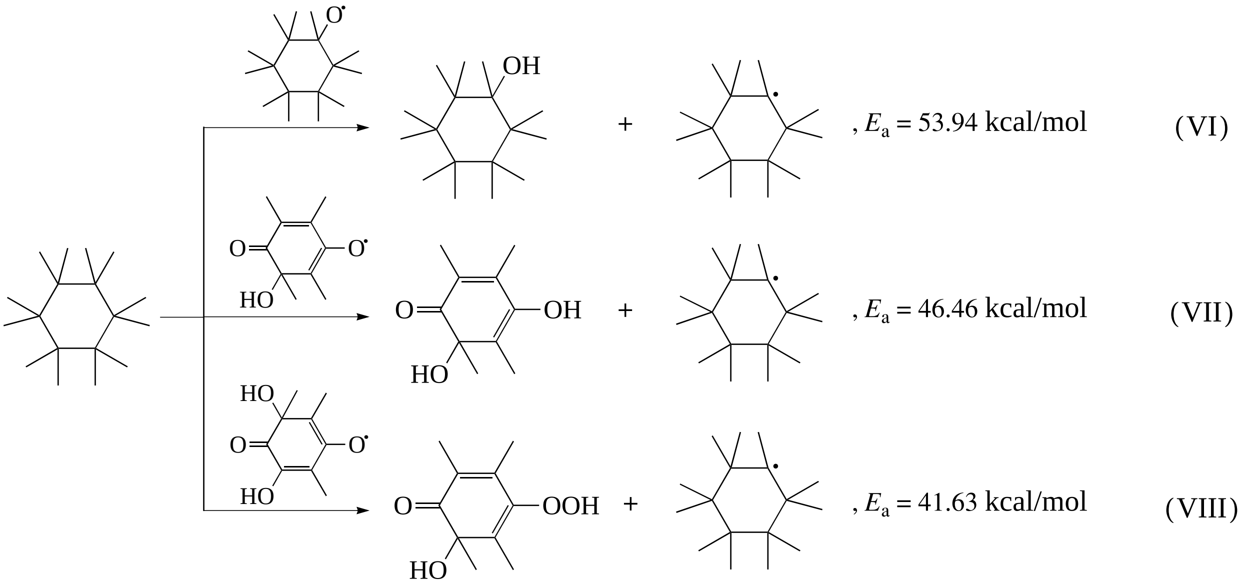
**Scheme 1**

Based on an analysis of the ratio between the reaction rates $w_3$ and $w_4$, which are given in Scheme 1,



$$= \frac{10^9 \times 10^{-3}}{10^9 \times 10^{-10}} \cong 10^7,$$

we can conclude that the contribution of reaction (IV), which leads to the formation of a hydroxy quinolide peroxide, to the overall rate of conversion of species **A** is almost equal to zero. Therefore, it is evident that the positive effect of Q additives on the oxidation of cyclohexane is due to the acceleration of chain propagation steps by species with a free valence (**A** and **B**). This follows from a comparison between the quantum-chemically calculated (PM3 method) activation energies of reactions (VI), (VII), and (VIII) (Scheme 2).



**Scheme 2**

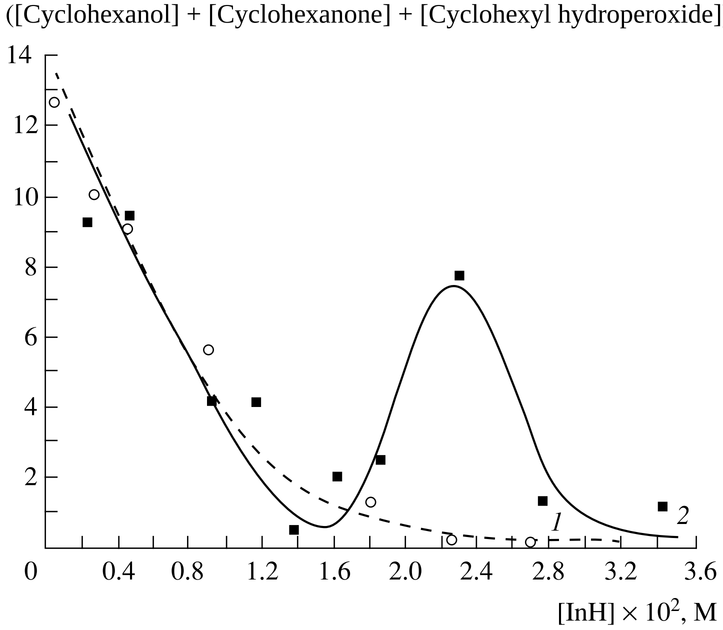
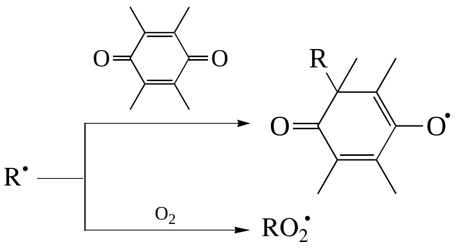


**Fig. 1.** Dependence of the total yield of the target products of cyclohexane oxidation in HOAc on the initial concentration of (*1*) hydroquinone or (*2*) quinone. $[\text{Cyclohexane}]_0 = 4.2$ M; $[\text{Co(OAc)}_2]_0 = 2.0 \times 10^{-3}$ M; $[H_2O_2]_0 = 1.0$ M; $t = 7$ h; 303 K.

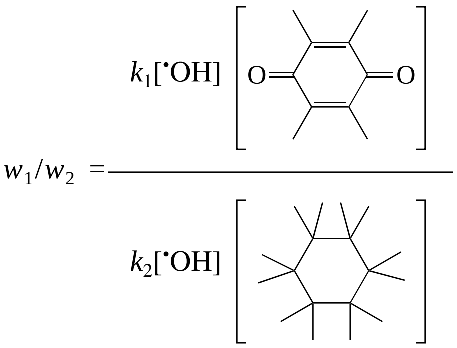
To determine each of the components (inhibiting and accelerating) of the effect of Q on the oxidation of cyclohexane, let us estimate the ratios between reaction rates $w_1/w_2$ and $w_9/w_{10}$ as follows:



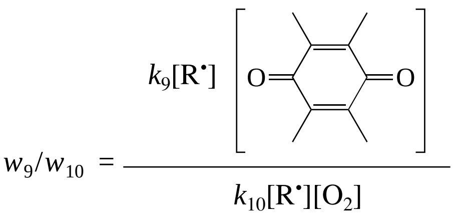
(IX)

(X)

$k_9 = (3–4) \times 10^9$ l mol$^{-1}$ s$^{-1}$ [21, 22]; $k_{10} = (0.5–5) \times 10^8$ l mol$^{-1}$ s$^{-1}$ [20], where $R^\bullet$ is the cyclohexyl radical.



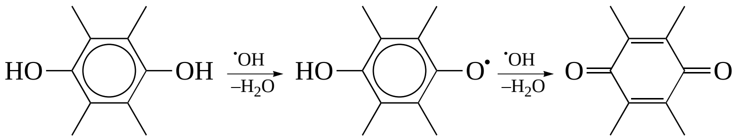
$$= \frac{10^9 \times 2 \times 10^{-2}}{10^8 \times 4.2} \cong 5 \times 10^{-2},$$



$$= \frac{10^9 \times 2.0 \times 10^{-2}}{10^8 \times 10^{-3}} \cong 2 \times 10^2.$$

Thus, although the rate of the reaction of hydroxyl radicals with hydroquinone molecules is as low as about 5% of the rate of hydrogen abstraction from cyclohexane molecules by these radicals (the $w_1/w_2$ ratio), less than 0.5% of the resulting cyclohexyl radicals were consumed in the formation of cyclohexyl peroxide radicals in the presence of quinone (the $w_9/w_{10}$ ratio). In contrast to phenols, quinone does not react with $RO_2^\bullet$ [21]; therefore, all of the resulting cyclohexyl peroxide radicals are converted into target products.

It is reasonable to conclude that free-radical species generated from quinone under reaction conditions can propagate the chain because the oxidation of cyclohexane in the presence of certain additives of this inhibitor was even accelerated, even though almost 100% of the cyclohexyl radicals were trapped by Q molecules. Based on the values of $E_a$ calculated for reactions (VI)–(VIII), the ratios between the rate constants $k_7/k_6$ and $k_8/k_6$ can be estimated at $10^2–10^5$. Thus, although the concentration of cyclohexyl radicals decreased with increasing concentration of Q, the overall rate of cyclohexane oxidation can increase because of an increase in the concentration of active species **A** and **B**; this results in an increase in the rate of chain propagation through reactions (VII) and (VIII). As the concentration of InH in the reaction mixture was further increased, all of the generated $R^\bullet$ radicals were trapped by inhibitor molecules, and the oxidation process was almost terminated. Only the inhibiting properties of HQ can be explained by the fact that $RO_2^\bullet$ radicals can also undergo decay (by analogy with phenols [23]) on this species.



(XI)

**D**

In the case of HQ, the free valence in the semiquinone radical **D** that is formed is delocalized at the conjugated bonds of the phenol ring. This delocalization decreases electron density on the terminal oxygen atom and, consequently, stabilizes this species.

To study the kinetics of formation and consumption of compounds capable of reducing $KMnO_4$, we performed experiments on the oxidation of inhibitors in the given catalytic system in the absence of cyclohexane. Note that both Q and HQ can be oxidized by $KMnO_4$.

An analysis of the kinetic curves shown in Fig. 2 allowed us to conclude that peroxide decomposition was almost completely inhibited in the presence of HQ. This manifests itself in the almost constant consumption (in time) of $KMnO_4$ for the titration of samples ($\tan\alpha \cong 0$) (Fig. 2, curves *2*, *3*). This can be explained by either the effective chain termination on hydroquinone molecules and the low activity of radicals resulting from HQ in hydrogen atom abstraction or the formation of the $InH\cdot\cdot Co(OAc)_2$ complexes ($k = 10^{-3}$ l $mol^{-1}$ $s^{-1}$ [20]), which result in catalyst deactivation and a decrease in the rate of $H_2O_2$ homolysis. In the case of using Q, a greater change in the consumption of $KMnO_4$ than that in the case of HQ was detected (Fig. 3). This can be considered as evidence for the interaction (consumption) of $H_2O_2$ with InH, the formation of $KMnO_4$-titrated peroxide compounds from Q, and the lower catalyst deactivation by this inhibitor. The possibility of formation of inhibitor–catalyst complexes was supported by a shift of the absorption band of an acetic acid solution of Q + $Co(OAc)_2$ to the short-wavelength region, as compared with the absorption spectrum of individual Q (Fig. 4, curves *1*, *3*) (the solutions of HQ and HQ + $Co(OAc)_2$ do not absorb in the visible region of the spectrum). The measurements of the electronic absorption spectra of an acetic acid solution of a mixture of $Co(OAc)_2$ + Q + $H_2O_2$ (in the visible region), a solution of individual Q, and a solution of a mixture of Q + $Co(OAc)_2$ (Fig. 4) revealed a dramatic increase in absorption intensity, which increased with time, and a hypsochromic shift of the maximum for the first solution (curves *4*–*6*), as compared with the second and third solutions (curves *1*, *3*). We explained this fact by the formation and accumulation of quinone oxidation products containing one or two hydroxyl groups with time.

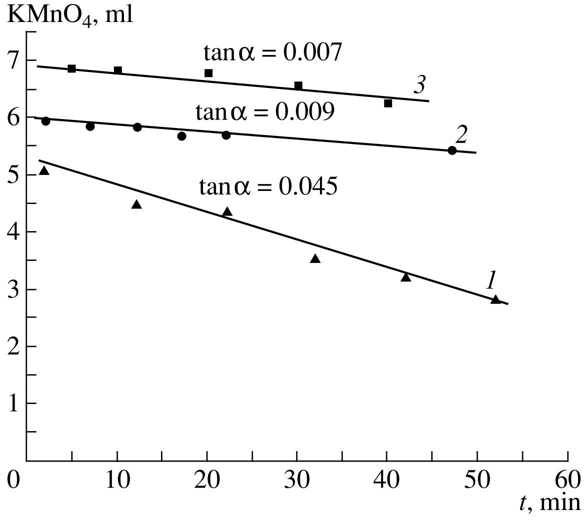


**Fig. 2.** Kinetics of $KMnO_4$ (0.02 N) consumption in the titration of oxidation product samples initially containing hydroquinone, M: (*1*) 0, (*2*) $0.5 \times 10^{-2}$, and (*3*) $1.0 \times 10^{-2}$. $[Cyclohexane]_0 = 0.0$ M; $[Co(OAc)_2]_0 = 2.0 \times 10^{-3}$ M; $[H_2O_2]_0 = 1.0$ M; solvent, HOAc; 303 K.

To determine the nature of the products formed in the course of Q oxidation in the test system, the oxidation products were analyzed by TLC. The following products that oxidized $I^-$ to $I_2$ were identified from the $R_f$ values by comparison with the retention factors of individual peroxides: $H_2O_2$ ($R_{f1} = 0.18$), cyclohexyl hydroperoxide ($R_{f2} = 0.75$), cyclohexyl α-ketohydroperoxide ($R_{f3} = 0.80$), and peroxycyclohexyl hydroperoxide ($R_{f4} = 0.90$) [24]. The presence of quinone in the reaction mixture resulted in the appearance of spots with $R_{f5} = 0.55$ (very weak) and $R_{f6} = 0.81$ in thin-layer chromatograms; these spots were attributed to unre-

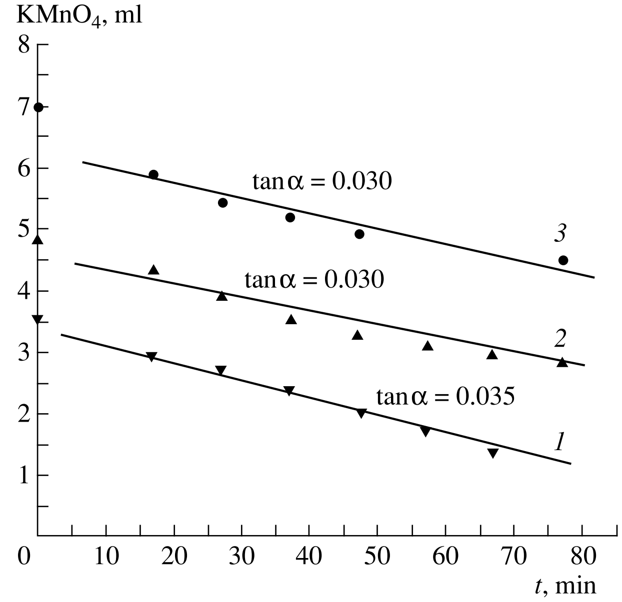


**Fig. 3.** Kinetics of $KMnO_4$ (0.02 N) consumption in the titration of oxidation product samples initially containing quinone, M: (*1*) 0, (*2*) $1.0 \times 10^{-2}$, and (*3*) $2.0 \times 10^{-2}$. [Cyclohexane]$_0$ = 0.0 M; $[Co(OAc)_2]_0 = 2.0 \times 10^{-3}$ M; $[H_2O_2]_0$ = 1.0 M; solvent, HOAc; 303 K.

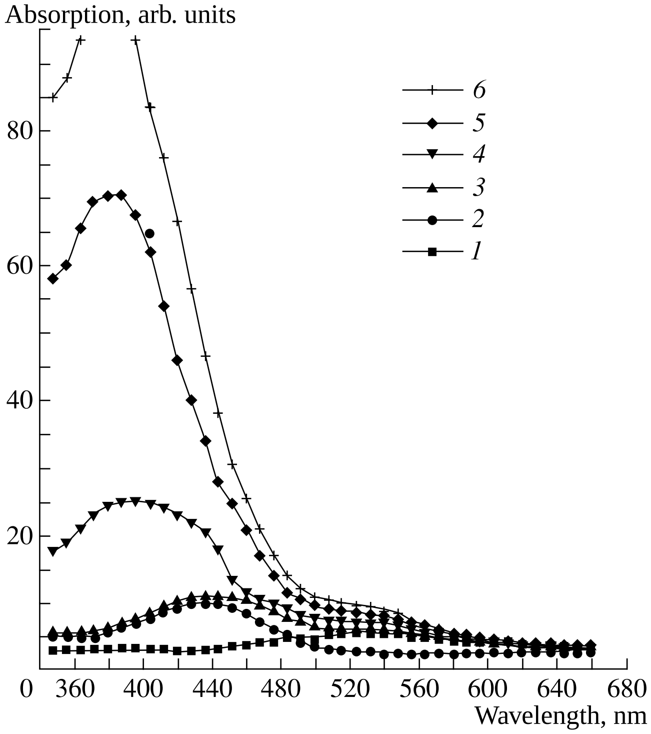


**Fig. 4.** Electronic absorption spectra of the acetic acid solutions: (*1*) $0.5 \times 10^{-2}$ M Q; (*2*) $1.5 \times 10^{-3}$ M $Co(OAc)_2$ + 0.1 M $H_2O_2$; (*3*) $1.5 \times 10^{-3}$ M $Co(OAc)_2$ + $0.5 \times 10^{-2}$ M Q; $0.5 \times 10^{-2}$ M Q + $0.5 \times 10^{-3}$ M $Co(OAc)_2$ + 0.10 M $H_2O_2$; (*4*) immediately after preparation; (*5*) 15 min after preparation; and (*6*) 30 min after preparation.

acted inhibitor (the spot with $R_{f6}$ overlapped that with $R_{f3}$; it was identified in a pure form in the oxidation products prepared in the absence of cyclohexane).

The presence of HQ in the starting reaction mixture did not cause the appearance of additional spots in the thin-layer chromatograms.

Let us consider the results of experiments on the inhibited oxidation of cyclohexane (Fig. 1) and compare them with the consumption of $KMnO_4$-reducing compounds that are formed in the test catalytic system during the oxidation of Q (Fig. 3). An analogy between an increase in the total yield of target products and changes in the consumption of permanganate may be noted.

As for the composition of cyclohexane oxidation products, in the case of Q, a lower relative concentration of cyclohexyl hydroperoxide was detected than that in the case of HQ (Tables 1, 2). This may be evidence for a more intense deactivation of the catalyst by hydroquinone than by quinone, which also affects the yield of target oxidation products.

The above results support the hypothesis about the possibility of chain propagation by species with a free valence, which are generated from quinone in the test oxidation system, and allow us to draw the following conclusions:

(1) Under conditions of liquid-phase oxidation of cyclohexane in the $HOAc–H_2O_2–Co(OAc)_2$ catalytic system, quinone at certain concentrations can propagate the hydrocarbon oxidation chain.

(2) Inhibition can be due to either the chain termination of $R^\bullet$ radicals on Q molecules or the deactivation of the catalyst as a result of its complexation with InH. Chain propagation occurs through the reaction of hydrogen-atom abstraction from the oxidized substrate molecule by mono- and dihydroxy-containing radicals, the derivatives of Q.

(3) Under the reaction conditions at all the concentrations studied, HQ exhibited only inhibiting properties, which can be explained by the nature of its interaction with free radicals.

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