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PEROXIDES-XI

Hydrogen Peroxide Formation in the Oxidation of Carbonyl-Containing Compounds at β-CH Bonds

Yu. V. Nepomnyashchikh, I. M. Nosacheva, and A. L. Perkel'

Kuzbass State Technical University, Kemerovo, Russia

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Abstract—The concepts of the selective inhibition of reactions with the participation of $HO_2^{\bullet}$ radicals by nitrobenzene in accordance with a cyclic mechanism were supported using cyclohexanol oxidation as an example. It was demonstrated that the nitroxyl radical generated from nitrobenzene selectively reacts with $HO_2^{\bullet}$ to form hydrogen peroxide and nitrobenzene. A decrease in the rates of oxidation of esters, carboxylic acids, and ketones with specially chosen structures in the presence of nitrobenzene, as well as the detection of H_2O_2 and corresponding α,β-unsaturated compounds among the reaction products, indicated that the degradation of β-peroxyl radicals of the above compounds occurred under conditions of the liquid-phase oxidation of organic substances that result in the formation of the $HO_2^{\bullet}$ radical and an unsaturated compound.

INTRODUCTION

Carbonyl-containing compounds (ketones, carboxylic acids, esters, and lactones) are formed as by-products in the oxidative degradation of hydrocarbons and their oxygen derivatives [1–3]. The subsequent conversion of these compounds is primarily related to radical chain oxidation at CH bonds, both neighboring to (α-) and distant from (β-, γ-, δ-, etc.) a functional group [1, 2, 4].

The oxidation of ketones at α-CH bonds (α-mechanism), which are activated by a factor of 12–16 greater than that of CH bonds of hydrocarbons [2], is usually considered as a predominant reaction. The reactivities and reaction mechanisms of hydroperoxides that are formed in the oxidation of ketones at β- or more distant CH bonds are taken equal to those of hydrocarbons [1]. It is likely that this assumption is not completely correct. The presence of the electron-acceptor C=O group in a ketone molecule leads to the deactivation of β- and γ-CH bonds, as it was observed in the oxidation of other compounds with electron-acceptor substituents: hexanoic acid [5], methyl hexanoate [5], cyclohexyl acetate [6], and cyclohexanol [7].

The importance of the α-mechanism decreases on going from the oxidation of ketones to the oxidation of carboxylic acids and acyl fragments of their esters, the reactivity of α-CH bonds in which is much lower than that in ketones [4]. Based on a study of the composition of products from the oxidation of hexanoic acid and methyl hexanoate (after reduction with $LiAlH_4$), Pritzkow and Voerckel [5] concluded that the reactivity of β-CH bonds of the acid and the acyl fragment of the ester is lower than that of the δ-CH bonds of these compounds by factors of 13.3 and 7.6, respectively. In this case, 2-pentanone was the only product the formation of which was related to the oxidation of the acid and the ester at β-CH bonds [5].

It is believed that this low reactivity of the β-CH bonds of an acid and the acyl fragment of its ester is associated with not only a deactivating effect of electron-acceptor substituents (–COOH and COOR) but also the occurrence of other reaction paths for the conversion of intermediates from the oxidation of these compounds at β-CH bonds.

Here, we report data on the effect of nitrobenzene on the kinetics of oxidation of structurally different esters, carboxylic acids, and ketones and on the detection of H_2O_2 and corresponding α,β-unsaturated carboxylic acids, esters, and ketones as the constituents of reaction products. These data are indicative of the degradation of the β-peroxyl radicals of the above carbonyl-containing products under conditions of the liquid-phase oxidation of organic substances that result in production of the $HO_2^{\bullet}$ radical and an unsaturated compound.

EXPERIMENTAL

Phenyl butanoate was prepared by the slow distillation of acetic acid from a mixture of phenol, butyric anhydride, and acetic anhydride. *para*-Toluenesulfonic acid was used as an acylation and transacylation catalyst. The phenyl butanoate synthesized was purified by vacuum rectification in a flow of argon in order to remove a phenyl acetate impurity. The purity of the ester was 99.1 ± 0.5% according to GLC data; T_b = 90°C (11 Torr) is consistent with the published value T_b = 85°C (8 Torr) [8]. Phenyl 2,2-dimethylpropanoate was prepared in a similar manner from phenol, pivalic acid, and acetic anhydride. According to GLC data, the ester content was 98.4 ± 0.3%, and $T_b = 80°C$ (10 Torr).

Butanoic acid and propanoic acid (both of reagent grade) were purified by rectification in a flow of argon. T_b = 162 and 141°C for butanoic and propanoic acids, respectively; according to published data [8], T_b = 163.25 and 141.0°C for butanoic and propanoic acids, respectively. Cyclohexanone (analytical grade) was purified through a bisulfite derivative in order to remove cyclohexanol and ether impurities. Before oxidation, γ-butyrolactone (reagent grade) was vacuum distilled in a flow of argon; $T_b = 93°C$ (21 Torr), which is consistent with a published value of 91–92°C (20 Torr) [8]. Cyclohexanol of analytical grade was purified in accordance with a published procedure [7]. According to GLC data, the purity of this substance was 99.5 ± 0.1%; the concentrations of cyclohexanol ethers and cyclohexanone were no higher than 0.01% (GLC) and lower than 0.003% (spectrophotometric determination as 2,4-dinitrophenylhydrazone), respectively. Nitrobenzene of chemically pure grade was dried with anhydrous $MgSO_4$ and distilled in a vacuum. The procedures used for the purification of azobisisobutyronitrile (AIBN) and chlorobenzene were described elsewhere [7].

Crotonic acid in oxidized butyric acid and methyl 2-hexenoate in oxidized methyl hexanoate were determined by GLC after conversion into methyl 2,3-dibromobutanoate and methyl 2,3-dibromohexanoate by quantitative bromination [9] followed by methylation with diazomethane.

Hydrogen peroxide in oxidized γ-butyrolactone was determined as the difference between the total peroxide concentration and the concentration of peroxides after the selective decomposition of H_2O_2 with catalase. In this case, the concentration of peroxide compounds was determined by colorimetry after sample treatment with a reagent containing Fe^{2+} ions and *N*,*N*-dimethyl-*para*-phenylenediamine [10].

The kinetics of gas absorption in the oxidation of cyclohexanol, carboxylic acids, esters, ketones, and γ-butyrolactone with molecular oxygen was measured on a manometric unit in the kinetic region of oxygen absorption. The samples of oxidized products, which were subsequently used for studying their composition, were prepared under the same conditions.

RESULTS AND DISCUSSION

The inhibiting effect of nitrobenzene in the oxidation of the propionates of pentaerythritol and 2,2-dimethylol-1-butanol was found previously [11, 12]. According to Martem'yanov *et al.* [11], nitrobenzene does not react with secondary and tertiary peroxyl radicals or with alkyl and alkoxyl radicals. Because this phenomenon was not observed in the acetates of these polyhydric alcohols, it was related to the interaction of nitrobenzene with α-hydroxy-α-alkoxyalkoxyl radical (**I**) ($R^1C(OR^2)(OH)O^{\bullet}$); according to Martem'yanov *et al.* [12], this radical is formed with the participation of the isomerization reactions of an ester peroxyl radical (intramolecular chain transfer). More recently, Borisov and coauthors [13, 14] clearly demonstrated that nitrobenzene selectively reacts with the $HO_2^{\bullet}$ radical rater than radical **I**. They related the inhibiting effect of nitrobenzene to cyclic chain termination in accordance with the reaction scheme accepted for other inhibitors, such as quinones [15]. At the first step, the reduction of nitrobenzene with hydroperoxyl radicals results in a nitroxyl radical, which is subsequently oxidized by a hydroperoxyl or peroxyl radical with the regeneration of nitrobenzene.

The above two reactions are hypothetical. At the same time, it is of importance to evaluate the probability and selectivity of these reactions for the correct interpretation of results obtained in studies of the effect of nitrobenzene on the kinetics of oxidation of organic reactions as a test for the $HO_2^{\bullet}$ radical. We believe that these data can be obtained in a material whose oxidation generates $HO_2^{\bullet}$ radicals. Among these materials are secondary alcohols, in the oxidation of which both α-hydroxyperoxyl radicals and $HO_2^{\bullet}$ radicals are oxidation chain carriers [1, 16].

Because in the oxidation of cyclohexanol the selectivity of oxidation at α-CH bonds is close to 98% [7, 16], the oxidation of cyclohexanol (R_2CHOH) initiated by cumyl hydroperoxide (R^1OOR^1) in the absence of nitrobenzene can be represented by the following reaction scheme:

$$R^1OOR^1 \longrightarrow 2R^1O^{\bullet}, \qquad \text{(I)}$$

$$R_2CHOH + R^1O^{\bullet} \longrightarrow R_2\dot{C}OH + R^1OH, \qquad \text{(II)}$$

$$R_2\dot{C}OH + O_2 \longrightarrow R_2C(OH)OO^{\bullet}\ (\mathbf{II}), \qquad \text{(III)}$$

$$R_2C(OH)OO^{\bullet} \longrightarrow R_2C{=}O + HO_2^{\bullet}, \qquad \text{(IV)}$$

$$HO_2^{\bullet} + R_2CHOH \longrightarrow H_2O_2 + R_2\dot{C}OH, \qquad \text{(V)}$$

$$\begin{array}{l} R_2C(OH)OO^{\bullet} + R_2CHOH \\ \longrightarrow R_2C(OH)OOH + R_2\dot{C}OH, \end{array} \qquad \text{(VI)}$$

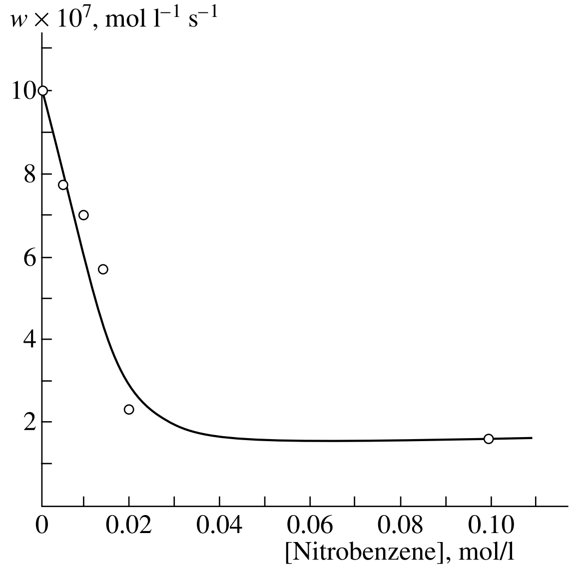
$$R_2C(OH)OOH \longrightarrow H_2O_2 + R_2C{=}O, \qquad \text{(VII)}$$

$$\begin{array}{l} HO_2^{\bullet} + R_2C(OH)OO^{\bullet} \\ 2HO_2^{\bullet} \\ 2R_2C(OH)OO^{\bullet} \end{array} \longrightarrow \left\}\begin{array}{l} \text{molecular} \\ \text{products.} \end{array}\right. \qquad \begin{array}{r} \text{(VIII)} \\ \text{(IX)} \\ \text{(X)} \end{array}$$

According to Borisov *et al.* [14], the following reactions also occur in the presence of nitrobenzene:

$$C_6H_5NO_2 + HO_2^{\bullet} \longrightarrow C_6H_5N(OH)O^{\bullet}\ (\mathbf{III}) + O_2, \quad \text{(XI)}$$

$$C_6H_5N(OH)O^{\bullet} + HO_2^{\bullet} \longrightarrow C_6H_5NO_2 + H_2O_2, \quad \text{(XII)}$$



Effect of the concentration of nitrobenzene on the rate of oxygen consumption in the cumyl hydroperoxide–initiated oxidation of a cyclohexanol solution (3.2 mol/l) in *ortho*-dichlorobenzene at 100°C; [cumyl hydroperoxide] = 0.01 mol/l.

$$C_6H_5N(OH)O^{\bullet} + R_2C(OH)OO^{\bullet} \longrightarrow C_6H_5NO_2 + R_2C(OH)OOH. \qquad \text{(XIII)}$$

These reactions compete with reactions (IV)–(VI) and (VIII)–(X), and their rates depend on nitrobenzene concentration.

The effect of nitrobenzene on the rate of oxygen absorption in the cumyl hydroperoxide–initiated oxidation of a cyclohexanol solution (3.2 mol/l) in *ortho*-dichlorobenzene at 100°C was studied over the concentration range 0–0.1 mol/l. The kinetic curves of oxygen absorption in the experiments with nitrobenzene were rectilinear, as in the experiment without nitrobenzene. An increase in the concentration of the nitro compound (figure) resulted in a decrease in the rate of alcohol oxidation to a value which reached a minimum at [nitrobenzene] > 0.03 mol/l; this minimum value was ~14.5% of the rate of oxidation in the experiment without nitrobenzene. Evidently, this is due to the attainment of a nitrobenzene concentration at which practically all the $HO_2^{\bullet}$ radicals are consumed by nitrobenzene and nitroxyl radical **III** in reactions (XI) and (XII), respectively, and α-hydroxyperoxyl radical **II** is an oxidation chain carrier.

To examine the completeness of nitrobenzene regeneration in the course of reactions (XI)–(XIII), we studied the cumyl hydroperoxide–initiated oxidation ($w_i = 3.46 \times 10^{-7}$ mol l^{-1} s^{-1}) of cyclohexanol at 110°C and [nitrobenzene] = (9.73 ± 0.05) × 10^{-3} mol/l. Although the nitrobenzene concentration used was lower than the limiting concentration of the nitro compound that provides the complete consumption of $HO_2^{\bullet}$ radicals, it allowed us to more accurately follow the possible consumption of the nitro compound. After oxidation for 13.5 h, 0.146 mol/l of oxygen was absorbed, and [nitrobenzene] remained practically unaffected and equal to (9.77 ± 0.06) × 10^{-3} mol/l; this fact is indicative of the complete regeneration of the nitro compound.

At the same time, the limiting character of the dependence of the rate of cyclohexanol oxidation on nitrobenzene concentration is inconsistent with reaction (XIII) of the cyclic inhibition scheme. Based on a quasisteady-state concentration of the nitroxyl radical, the rate of its formation is equal to the rate of consumption:

$$\frac{d[C_6H_5N(OH)O^{\bullet}]}{d\tau} = k_{11}[C_6H_5NO_2][HO_2^{\bullet}] - k_{12}[C_6H_5N(OH)O^{\bullet}][HO_2^{\bullet}] - k_{13}[C_6H_5N(OH)O^{\bullet}][R_2C(OH)O_2^{\bullet}] = 0.$$

The rate of reaction (XI) should increase with an increase in [nitrobenzene]; as a consequence, the concentration of nitroxyl radical **III** should increase. In turn, the latter circumstance should result in an increase in the rate of reaction (XIII) and thereby in a decrease in the rate of oxidation. Consequently, reaction (XIII) is improbable, and cyclic chain termination occurs in reactions (XI) and (XII).

An experimental technique with the use of nitrobenzene as a selective inhibitor was used for evaluating the role of $HO_2^{\bullet}$ radicals in the course of oxidation of the main types of carbonyl-containing oxidation products: ketones, carboxylic acids, esters, and γ-lactones. The structure of test materials was chosen so that it provided maximally full information on the mechanism of formation of $HO_2^{\bullet}$ radicals.

We studied the effect of nitrobenzene (0.1 mol/l) on the kinetics of oxygen absorption in the cumyl hydroperoxide-initiated and AIBN-initiated oxidation of cyclohexanone, 1-phenyl-1-butanone, butanoic acid, propanoic acid, phenyl butanoate, phenyl 2,2-dimethylpropanoate, and γ-butyrolactone. Table 1 summarizes the experimental conditions and results.

As in the oxidation of cyclohexanol, the kinetic curves of oxygen absorption in experiments with and without nitrobenzene were rectilinear. Except for phenyl 2,2-dimethylpropanoate and ketones, the addition of nitrobenzene considerably (although to a smaller degree than in the oxidation of the alcohol) decreased the rate of oxygen absorption (Table 1); this suggests the formation of the $HO_2^{\bullet}$ radical in the oxidation of the other compounds. Thus, it can be seen in Table 1 that $HO_2^{\bullet}$ radicals are formed not only in the oxidation of esters, as demonstrated by Borisov *et al.* [14], but also

Table 1. Effect of nitrobenzene on the rates of oxidation of the carbonyl-containing oxidation products of organic substances

Oxidized substance	T, °C	[RH], mol/l	$w \times 10^6$, mol l^{-1} s^{-1}	$w_{NB} \times 10^6$, mol l^{-1} s^{-1}	$\frac{w - w_{NB}}{w}$
Phenyl butanoate*	100	6.3	1.4 ± 0.1	1.1 ± 0.1	0.21
Phenyl-2,2-dimethylpropanoate*	134	3.7	2.4 ± 0.2	2.4 ± 0.2	0
Butanoic acid*	110	4.0	3.1 ± 0.2	1.5 ± 0.2	0.52
Propanoic acid*	135	13.4	2.8 ± 0.2	2.1 ± 0.3	0.25
1-Phenyl-1-butanone**	65	6.7	1.0 ± 0.1	0.9 ± 0.1	0.1
Cyclohexanone**	70	10.2	1.0 ± 0.2	0.8 ± 0.2	0.2
γ-Butyrolactone*	120	8.8	5.1 ± 0.3	1.4 ± 0.2	0.72

Note: w and w_{NB} are the rates of oxygen consumption in the absence and in the presence of nitrobenzene, respectively.
* [Cumyl hydroperoxide] = 0.006 mol/l.
** [AIBN] = 0.06 mol/l.

in the course of oxidation of carboxylic acids and γ-butyrolactone. In the case of 1-phenyl-1-butanone and cyclohexanone, the effect is within the limits of experimental error (Table 1); therefore, a decrease in the rate of oxygen absorption for these compounds in the presence of nitrobenzene cannot be conclusive evidence for the formation of the $HO_2^{\bullet}$ radical.

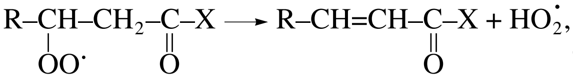
A constant difference between the rates of oxygen absorption in experiments without nitrobenzene (w) and with a nitrobenzene additive (w_{NB}) in the course of all the experiments is indicative of the generation of $HO_2^{\bullet}$ at a constant rate. It is most likely that the $HO_2^{\bullet}$ radicals are generated from peroxyl radicals rather than H_2O_2:

$$H_2O_2 + RO_2^{\bullet} \longrightarrow HO_2^{\bullet} + ROOH \qquad (XIV)$$

The subsequent interaction of $HO_2^{\bullet}$ with a substrate results in hydrogen peroxide:

$$HO_2^{\bullet} + RH \longrightarrow H_2O_2 + R^{\bullet} \qquad (XV)$$

A comparison between the structure peculiarities of oxidized compounds and the corresponding values of $\frac{w - w_{NB}}{w}$ and the absence of an effect in the oxidation of the acetates of polyhydric alcohols [11–14] demonstrate that the formation of $HO_2^{\bullet}$ occurred only if α- and β-CH bonds were simultaneously present at the carbonyl group. A decrease in the $\frac{w - w_{NB}}{w}$ ratio on going from γ-butyrolactone, esters, and carboxylic acids to ketones, in which α-CH bonds are considerably activated toward a radical attack, as well as on going from butanoic acid to propanoic acid, suggests that the $HO_2^{\bullet}$ radical is formed from β-carbonyl-containing peroxyl radicals with the participation of α-CH bonds:



$$\mathrm{R{-}\underset{\underset{OO^{\bullet}}{|}}{C}H{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}X \longrightarrow R{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}X + HO_2^{\bullet},} \qquad (XVI)$$

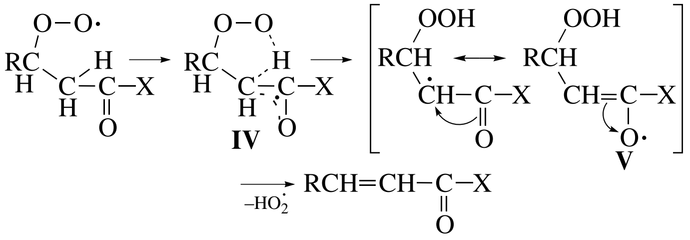
$$X = OH, OR, \text{or } R.$$

Reactions (XV) and (XVI) imply the formation of α, β-unsaturated esters, carboxylic acids, ketones, and hydrogen peroxide in the oxidation of the test compounds.

Indeed, methyl 2-hexenoate, crotonic acid, and 2-cyclohexenone were detected in the oxidation products of methyl hexanoate (60°C; [AIBN] = 0.01 mol/l), butanoic acid (130°C; [cumyl hydroperoxide] = 0.01 mol/l), and cyclohexanone (70°C; [AIBN] = 0.02 mol/l), respectively (Table 2).

The oxidation of γ-butyrolactone initiated by cumyl hydroperoxide (0.01 mol/l) at 119°C occurred in a chain mode. After oxidation for 3.5 h, $(4.9 \pm 0.2) \times 10^{-4}$ mol/l H_2O_2 was detected in the reaction medium; this was 27.4% of the total concentration of peroxide compounds.

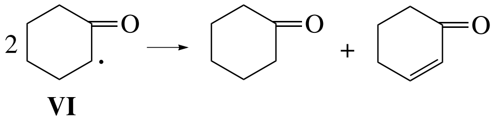
The mechanism of degradation of β-carbonyl-containing peroxyl (and α-hydroxyperoxyl) radicals into a ketone and $HO_2^{\bullet}$ in the absence of bases is not clearly understood. It is believed that it includes hydrogen 1,4-shift from the α-carbon atom to oxygen with the formation of carbon-centered radical **V** and the decomposition of this radical into an unsaturated compound and $HO_2^{\bullet}$:



(XVII)

It is believed [17] that hydrogen 1,4-shift is less probable than 1,5- or 1,6-shift because in the former case the most favorable linear structure O- - -H- - -C is difficult to reach in the transition state. However, if the CH bond at the α-position with respect to the carbonyl group participates in the transition state, transition state **IV** and radical **V** can be additionally stabilized by the delocalization of an unpaired electron on the carbonyl group. It is well known that a transition state with the participation of peroxyl radicals is closer to the end point [18], that is, radical **V**. The formation of a conjugated system of double bonds is favorable for the conversion of radical **V** into an unsaturated compound.

Kovalenko *et al.* [19] found that 2-cyclohexenone was formed in 1–2% yield in the oxidation of cyclohexane at 145–190°C. They assumed that it was formed by the disproportionation of two 2-oxocyclohexyl radicals **VI**

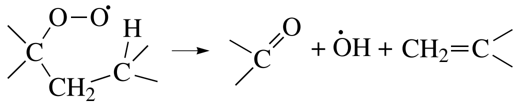


VI

(XVIII)

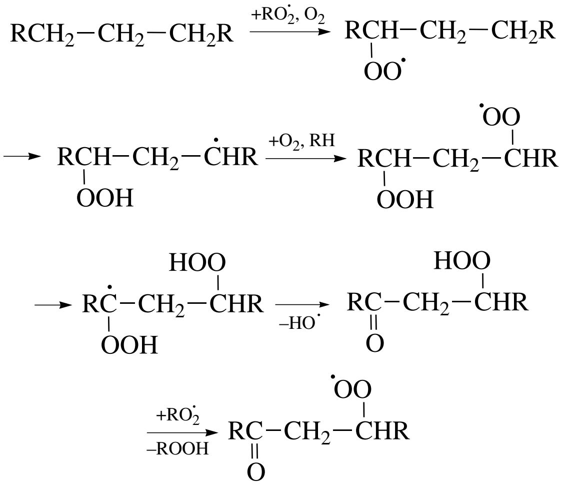
The probability of reaction (XVIII) under conditions of cyclohexane oxidation is extremely low because of the low concentration of alkyl radicals in the presence of oxygen and the predominance of cyclohexyl radicals over them. The second possible path of 2-cyclohexenone formation, the elimination of water from 2-hydroxycyclohexanone, is also improbable because of an enhanced stability of α-ketoalcohols to dehydration [16]. Therefore, it is believed that this unsaturated ketone is primarily formed in a reaction like reaction (XVI).

Trofimova *et al.* [20] found that, in the oxidation of pentadecane at 130°C, unsaturated compounds were formed as a result of the unimolecular degradation of peroxyl radicals; they proposed a mechanism for the formation of unsaturated compounds, which included the degradation of a C–C bond



(XIX)

The role of β-carbonyl-containing peroxyl radicals in the formation of unsaturated compounds seems preferable if it is believed that these radicals not only result from the oxidation of carbonyl-containing products but also are formed in the course of oxidation of saturated hydrocarbons with the participation of intramolecular chain-transfer reactions:



$$\mathrm{RCH_2{-}CH_2{-}CH_2R} \xrightarrow{+\mathrm{RO_2^{\bullet}},\ \mathrm{O_2}} \mathrm{R\underset{OO^{\bullet}}{CH}{-}CH_2{-}CH_2R}$$

$$\longrightarrow \mathrm{R\underset{OOH}{CH}{-}CH_2{-}\dot{C}HR} \xrightarrow{+\mathrm{O_2},\ \mathrm{RH}} \mathrm{R\underset{OOH}{CH}{-}CH_2{-}\overset{^{\bullet}OO}{CH}R}$$

$$\longrightarrow \mathrm{R\underset{OOH}{\dot{C}}{-}CH_2{-}\overset{HOO}{CH}R} \xrightarrow[-\mathrm{HO^{\bullet}}]{} \mathrm{R\underset{\|\atop O}{C}{-}CH_2{-}\overset{HOO}{CH}R} \qquad \text{(XX)}$$

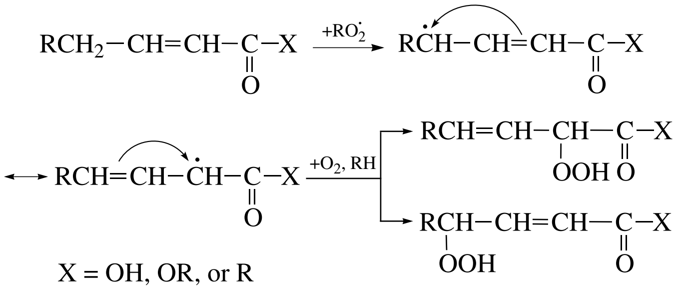
$$\xrightarrow[-\mathrm{ROOH}]{+\mathrm{RO_2^{\bullet}}} \mathrm{R\underset{\|\atop O}{C}{-}CH_2{-}\overset{^{\bullet}OO}{CH}R}$$

The α,β-unsaturated analogs formed in the oxidation of esters, carboxylic acids, lactones, and ketones

Table 2. Determination of unsaturated compounds in oxidized carbonyl-containing products ($n = 8$; $P = 0.95$)

Oxidized compound	Analyte	Oxidation time, h	Found	
			$C \times 10^3$, mol/l	s_r
Methyl hexanoate	Methyl 2-hexenoate	10	1.37 ± 0.07	0.06
Butanoic acid	Crotonic acid	2	0.83 ± 0.04	0.05
		3	1.18 ± 0.04	0.04
Cyclohexanone	2-Cyclohexenone	6.5	0.21 ± 0.01	0.07

belong to the most easily oxidizable organic compounds because they contain a double bond. Their reactions at allyl CH bonds result in two unsaturated hydroperoxides:



$$\mathrm{RCH_2{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}X} \xrightarrow{+\mathrm{RO_2^{\cdot}}} \mathrm{R\dot{C}H{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}X} \longleftrightarrow \mathrm{RCH{=}CH{-}\dot{C}H{-}\underset{\underset{O}{\|}}{C}{-}X} \xrightarrow{+\mathrm{O_2,\ RH}} \mathrm{RCH{=}CH{-}\underset{\underset{OOH}{|}}{C}H{-}\underset{\underset{O}{\|}}{C}{-}X} + \mathrm{R\underset{\underset{OOH}{|}}{C}H{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}X}$$

X = OH, OR, or R

(XXI)

Either of these peroxides can be converted into corresponding unsaturated alcohols or ketones with functional groups at the 2- or 4-positions rather than the 3-position. This circumstance should be taken into account when interpreting data on the composition of oxidation products for evaluating the reactivity at the 2-, 3-, and 4-positions with respect to the carbonyl group. It is of importance that the polymerization of unsaturated intermediates under the action of free radicals can be the source of resinous products; therefore, the selectivity of oxidation processes can be decreased.

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