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Kinetics and Mechanism of the Liquid-Phase Oxidation of *tert*-Butyl Phenylacetate

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Abstract—The oxidation of *tert*-butyl phenylacetate in *ortho*-dichlorobenzene at 140°C occurs with short chains. The primary nonperoxide reaction products (*tert*-butyl α-hydroxyphenylacetate, *tert*-butyl α-oxophenylacetate, and benzaldehyde) are formed by the decomposition of a hydroperoxide (*tert*-butyl α-hydroperoxyphenylacetate) and (or) by the recombination of peroxy radicals with and without chain termination. Benzaldehyde and *tert*-butyl α-hydroxyphenylacetate undergo radical chain oxidation in a reaction medium to result in benzoic acid and *tert*-butyl α-oxophenylacetate. Homolytic hydroperoxide decomposition is responsible for process autoacceleration and results in benzaldehyde, which is also formed from hydroperoxide by a nonradical mechanism, probably, via a dioxetane intermediate. Both of the reactions are catalyzed by benzoic acid. Benzoic acid has no effect on hydroperoxide conversion into *tert*-butyl α-oxophenylacetate, which most likely occurs as a result of hydroperoxide decomposition induced by peroxy radicals. The rate constants of the main steps of the process and kinetic parameters have been calculated by solving an inverse kinetic problem.

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Ester products are widely used as solvents, plasticizers, and lubricating oil components in chemical industry and technology. They are formed as by-products in the liquid-phase oxidation reactions of hydrocarbons and their oxygen derivatives [1–4]. In these reactions, as well as in the course of the thermooxidative decomposition of the above products, esters undergo various oxidative reactions, the specifics of which depend on the presence of an electron-acceptor group. This group affects the closest CH bonds of both acyl and alkoxy molecular fragments [4, 5]. The presence of several reaction sites in an ester molecule significantly complicates the reaction kinetics; the mechanisms of conversion of intermediate products are difficult to study because the same compounds can often be obtained via several reaction paths. Therefore, adequately reliable information on the kinetics and mechanisms of the oxidative reactions of esters at α-CH bonds can be obtained only by studying compounds with specially chosen structures [4], such as benzyl benzoate [6], benzyl phenylacetate [7], and *tert*-butyl phenylacetate [8]. In this work, we used *tert*-butyl phenylacetate in order to study the kinetics and mechanisms of the oxidative decomposition of the ester functional group at the α-CH bonds of an acyl fragment.

EXPERIMENTAL

tert-Butyl phenylacetate was prepared by the acylation of *tert*-butanol with phenylacetyl chloride in a pyridine medium. It was purified by vacuum rectification, bp 123–124°C (15 Torr). According to GLC data, the purity of the substance was no worse than 99.7 ± 0.2%. *ortho*-Dichlorobenzene was purified in accordance with a previously published procedure [8].

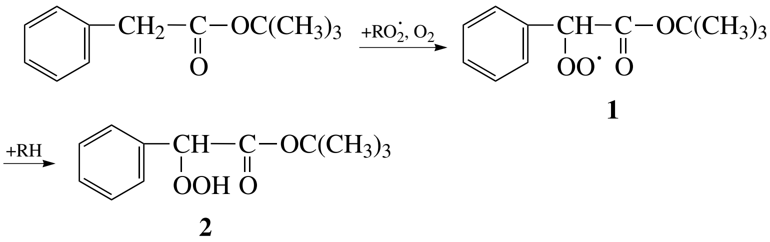
The ester was oxidized with air in a bubbler-type glass reactor in the kinetic region of oxygen consumption. The temperature was maintained to within ±0.2 K.

The total concentration of peroxide compounds was determined by iodometric titration. Peroxybenzoic acid was determined by GLC from the yields of diphenyl sulfoxide and diphenyl sulfone, the products of diphenyl sulfide oxidation by a peroxy acid [9]. The other products were determined by GLC. The methods used for the identification of reaction products and the conditions of sample treatment and GLC separation were reported elsewhere [8].

The unknown parameters of rate equations were calculated using a program based on the least-squares method in Delphi 5.5. A set of differential equations was solved using the fourth-order Runge–Kutta method at each particular step.

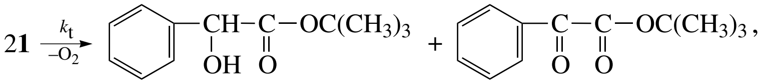
RESULTS AND DISCUSSION

tert-Butyl phenylacetate (a 1.5 M solution in *ortho*-dichlorobenzene) was oxidized with air at 140°C. Figure 1 shows the experimental concentrations of reaction products (peroxide compounds (primarily *tert*-butyl α-hydroperoxyphenylacetate), *tert*-butyl α-hydroxyphenylacetate, *tert*-butyl α-oxophenylacetate, benzaldehyde, benzoic acid, and peroxybenzoic acid) and the total concentration of reaction products. It can be seen in Fig. 1 that the first four products began to accumulate simultaneously; then, they were formed in consecutive–parallel reactions. *tert*-Butyl α-hydroperoxyphenylacetate is the primary molecular product of the radical chain oxidation of *tert*-butyl phenylacetate:



(I)

At the early stages of oxidation, *tert*-butyl α-hydroxyphenylacetate, *tert*-butyl α-oxophenylacetate, and benzaldehyde are primarily formed by the recombination of peroxy radicals **1** with chain termination (by the Russell mechanism) and without chain termination [8]:



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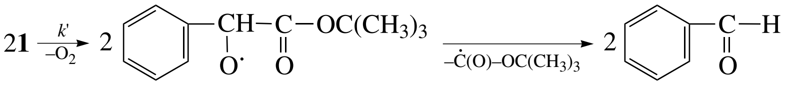
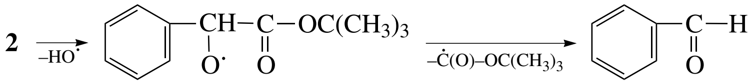


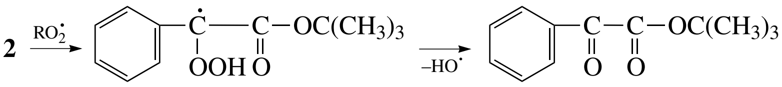
(III)

As *tert*-butyl α-hydroperoxyphenylacetate was accumulated in the reaction medium, the reaction paths of benzaldehyde and *tert*-butyl α-oxophenylacetate formation related to hydroperoxide decomposition became important. The homolytic reaction path resulted in benzaldehyde rather than *tert*-butyl α-hydroxyphenylacetate [8]:



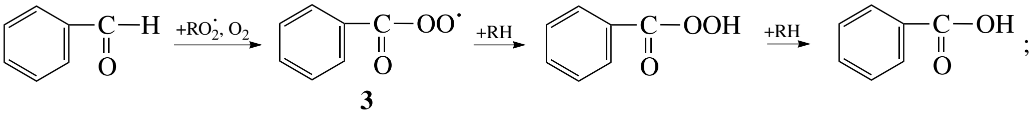
(IV)

One of the probable mechanisms of keto ester formation seems to be the hydroperoxide decomposition induced by free radicals [8]

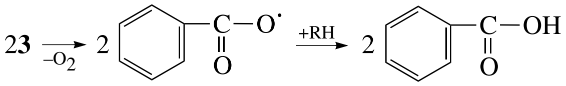


(V)

The presence of benzoic acid among the reaction products and the consecutive buildup of benzoic acid with benzaldehyde suggest that the source of the acid is the oxidation reaction of benzaldehyde, which is formed in reactions (III) and (IV). The conversion of benzaldehyde into benzoic acid can occur either through peroxybenzoic acid (reaction (VI)) (indeed, it was detected among the oxidation products) or through acylperoxy radicals (reaction (VII)) [10]:

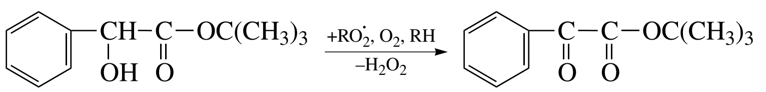


(VI)



(VII)

The radical chain oxidation of *tert*-butyl α-hydroxyphenylacetate to form *tert*-butyl α-oxophenylacetate can also occur:


(VIII)

Thus, the set of reactions that occur in the oxidation of *tert*-butyl phenylacetate can be represented by the following kinetic scheme:

$$\begin{tikzcd} RH \arrow[r] & RO_2^{\bullet} \arrow[r, "k_p"] \arrow[d, no head] & ROOH \arrow[r, "k_1^{эф}"] \arrow[d, "k_2^{ef}"] & R^1R^2C{=}O \\ R^1R^2C{=}O & {} \arrow[l, "k_t"'] \arrow[r, "k'"] & R^1CHO \arrow[r, "k'_p"] & R^1COOH \\ + & & & \\ R^1R^2CHOH \arrow[r, "k''_p"] & R^1R^2C{=}O. & & \end{tikzcd} \quad \text{(IX)}$$

The kinetics of reactions (I)–(VIII) can be described by the following set of equations:

$$-\frac{d[RH]}{d\tau} = k_p(2k_t)^{-0.5}[RH](w_i^0 + k_i^{ef}[ROOH])^{0.5} + (1 + k'/k_t)(w_i^0 + k_i^{ef}[ROOH]); \quad (1)$$

$$\frac{d[ROOH]}{d\tau} = k_p(2k_t)^{-0.5}[RH](w_i^0 + k_i^{ef}[ROOH])^{0.5} - (k_1^{ef} + k_2^{ef})[ROOH]; \quad (2)$$

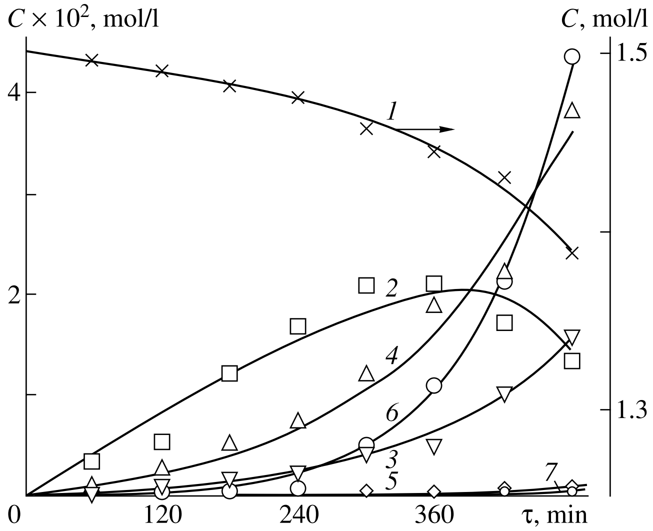


Fig. 1. Experimental concentrations and calculated curves of (*1*) ester consumption and (*2–7*) reaction product buildup in an experiment on the oxidation of a 1.5 M *tert*-butyl phenylacetate solution in *ortho*-dichlorobenzene at 140°C: (*1*) *tert*-butyl phenylacetate, (*2*) *tert*-butyl α-hydroperoxyphenylacetate, (*3*) *tert*-butyl α-oxophenylacetate, (*4*) benzaldehyde, (*5*) *tert*-butyl α-hydroxyphenylacetate, (*6*) benzoic acid, and (*7*) peroxybenzoic acid.

$$\frac{d[R^1R^2C{=}O]}{d\tau} = k_1^{ef}[ROOH] + 0.5(w_i^0 + k_i^{ef}[ROOH]) + k''_p(2k_t)^{-0.5}[R^1R^2CHOH](w_i^0 + k_i^{ef}[ROOH])^{0.5}; \quad (3)$$

$$\frac{d([RCHO] + [RCOOH])}{d\tau} = k_2^{ef}[ROOH] + k'/k_t(w_i^0 + k_i^{ef}[ROOH]); \quad (4)$$

$$\frac{d[RCHO]}{d\tau} = k_2'^{ef}[ROOH] + k'/k_t(w_i^0 + k_i^{ef}[ROOH]) - k'_{ie}(2k_t)^{-0.5}[RCHO](w_i^0 + k_i^{ef}[ROOH])^{0.5}; \quad (5)$$

$$\frac{d[R^1R^2CHOH]}{d\tau} = 0.5(w_i^0 + k_i^{ef}[ROOH]) - k''_p(2k_t)^{-0.5}[R^1R^2CHOH](w_i^0 + k_i^{ef}[ROOH])^{0.5}; \quad (6)$$

$$\frac{d[RCOOH]}{d\tau} = k''_p(2k_t)^{-0.5}[RCHO](w_i^0 + k_i^{ef}[ROOH])^{0.5}; \quad (7)$$

$$[RH]_0 - [RH] = [ROOH] + [R^1R^2C{=}O] + [R^1R^2CHOH] + [RCHO] + [RCOOH], \quad (8)$$

where k_p, k'_p, and k''_p are the reaction rate constants of chain propagation; k_t and k' are the reaction rate constants of the quadratic recombination of peroxy radicals with and without chain termination, respectively; k_i^{ef} is the rate constant of initiation due to hydroperoxide decomposition; w_i^0 is the rate of chain initiation; k_1^{ef} and k_2^{ef} are the effective rate constants of the steps of scheme (IX); [RH], [ROOH], [$R^1R^2C{=}O$], [R^1R^2CHOH], [RCHO], and [RCOOH] are the concentrations (mol/l) of *tert*-butyl phenylacetate, *tert*-butyl α-hydroperoxyphenylacetate, *tert*-butyl α-oxophenylacetate, *tert*-butyl α-hydroxyphenylacetate, benzaldehyde, and benzoic acid, respectively.

The oxidizability parameter of *tert*-butyl phenylace-

Calculated rate constants and kinetic parameters for the oxidation of a 1.5 M *tert*-butyl phenylacetate solution in *ortho*-dichlorobenzene at 140°C

Parameter	Calculated value
$k'_p(2k_t)^{-0.5}$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$	0.164
$k''_p(2k_t)^{-0.5}$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$	0.757
$w_i^0 \times 10^7$, mol l^{-1} s^{-1}	9.5
k'/k_t	2.24
$k_i^{ef} \times 10^3$, s^{-1}	$3.67 \times 10^{-3} + 2.39$ [RCOOH]
$k_1^{ef} \times 10^6$, s^{-1}	7.45
$k_2^{ef} \times 10^3$, s^{-1}	$3.02 \times 10^{-2} + 9.38$ [RCOOH]
$k_2^{'ef} \times 10^3$, s^{-1}*	$3.06 \times 10^{-3} + 1.99$ [RCOOH]
$k_2^{''ef} \times 10^3$, s^{-1}**	$2.71 \times 10^{-2} + 7.39$ [RCOOH]

* Reaction (IV).

** Reaction (X).

tate, which was determined in the temperature range 100–130°C, is expressed by the equation [8]

$$\log k_p(2k_t)^{-0.5} = (1.4 \pm 0.9) - (31.9 \pm 6.5)\ \text{kJ/mol}/2.303RT. \qquad (9)$$

Hence, it follows that, at 140°C, $k_p(2k_t)^{-0.5} = 2.57 \times 10^{-3}$ $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$.

Because hydroperoxide decomposition reactions are generally prone to acid catalysis in accordance with published data [1, 11], we assumed that the corresponding effective constants can depend on the concentration of benzoic acid:

$$k_i^{ef} = k_i + k'_i[\text{RCOOH}]. \qquad (10)$$

The table summarizes the constants of Eqs. (1)–(8) and (10) and kinetic parameters obtained by solving an inverse kinetic problem, and Fig. 1 shows the calculated curves.

It can be seen in Fig. 1 that the calculated curves adequately describe experimental points (the sum of squares of deviations is 1.42×10^{-4}).

A comparison of oxidizability parameters for benzaldehyde and *tert*-butyl α-hydroxyphenylacetate (see the table) with the oxidizability parameter of *tert*-butyl phenylacetate, which was calculated from Eq. (9), indicates that the reactivity of CH bonds in the first two compounds is much higher than that of the ester. This circumstance is consistent with the concept that aldehydes and the α-CH bonds of alcohols are highly reactive [1].

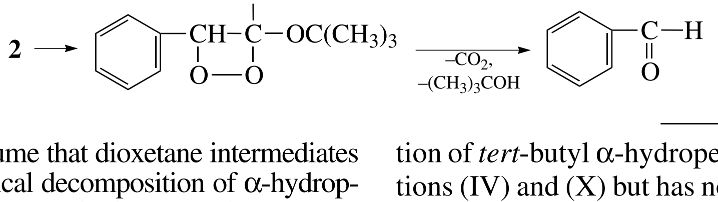
The ratio between the reaction rate constants of recombination of the peroxy radicals of *tert*-butyl phenylacetate without and with chain termination (k'/k_t = 2.24) is somewhat higher than that in the oxidation of this ester at 100°C (k'/k_t = 1.08 [8]). This is likely due to the fact that the role of the former reaction increases with temperature.

On the assumption that the autoacceleration of the process is related to homolytic hydroperoxide decomposition in reaction (IV), k_i^{ef} is related to k_2^{ef} by the equation

$$k_i^{ef} = 2ek_2^{ef}, \qquad (11)$$

where *e* is the coefficient of radical escape from a solvent cage; this coefficient is equal to 0.6 for aromatic solvents [12].

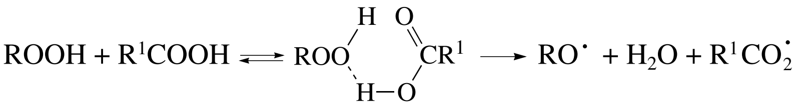
At [RCOOH] = 0, substitution of the obtained value of $k_i^{ef} = 2.2 \times 10^{-4}$ s^{-1} (table) into Eq. (11) results in $k_2^{ef} = 1.8 \times 10^{-4}$ s^{-1}, which is only ~10% of the calculated value (see the table). This circumstance indicates that, in addition to reaction (IV), a nonradical reaction path of benzaldehyde formation from *tert*-butyl α-hydroperoxyphenylacetate should exist. For example, benzaldehyde can be formed via a dioxetane intermediate that results from the intramolecular nucleophilic addition of the hydroperoxide group at the carbonyl group:



(X)

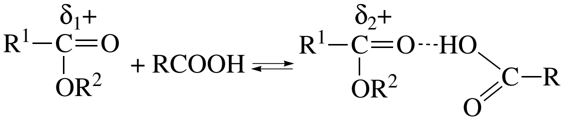
It is reasonable to assume that dioxetane intermediates are formed in the nonradical decomposition of α-hydroperoxy ketones and α-hydroxy-α-hydroperoxy ketones [2].

Benzoic acid, which is formed upon the oxidation of *tert*-butyl phenylacetate, accelerates the decomposition of *tert*-butyl α-hydroperoxyphenylacetate by reactions (IV) and (X) but has no effect on reaction (V) (see the table and Fig. 2). It is well known [11, 12] that carboxylic acids accelerate the homolytic decomposition of hydroperoxides in reactions like



$$\mathrm{ROOH} + \mathrm{R^1COOH} \rightleftharpoons \mathrm{ROO}\overset{\mathrm{H\quad O}}{\underset{\mathrm{H-O}}{\qquad}}\mathrm{CR^1} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{H_2O} + \mathrm{R^1CO_2^{\bullet}} \qquad \text{(XI)}$$

Benzoic acid has the greatest effect on reaction (X) (see the table and Fig. 2). In this case, it is evident that acid catalysis is related to the formation of acid–hydroperoxide complex **4**. The reactivity of this complex toward a nucleophilic attack of a hydroperoxide is higher than that of the free ester ($\delta_2+ > \delta_1+$):



$$\mathrm{R^1-}\overset{\delta_1+}{\underset{\mathrm{OR^2}}{\mathrm{C}}}\mathrm{=O} + \mathrm{RCOOH} \rightleftharpoons \mathrm{R^1-}\overset{\delta_2+}{\underset{\mathrm{OR^2}}{\mathrm{C}}}\mathrm{=O\cdots HO-C(=O)-R} \qquad \text{(XII)}$$

4

It is of importance that benzoic acid has no effect on reaction (V), and this is consistent with the proposed mechanism of keto ester formation.

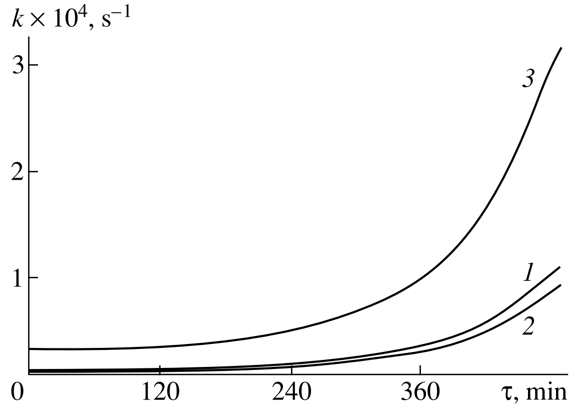


Fig. 2. Dependence of the effective rate constants of (*1*) initiation reactions in the decomposition of *tert*-butyl α-hydroperoxyphenylacetate and the (*2*) homolytic and (*3*) nonradical decomposition of *tert*-butyl α-hydroperoxyphenylacetate to benzaldehyde on the duration of oxidation.

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