Russian Journal of Applied Chemistry, Vol. 78, No. 3, 2005, pp. 443–447. Translated from Zhurnal Prikladnoi Khimii, Vol. 78, No. 3, 2005, pp. 447–451.
Original Russian Text Copyright © 2005 by Nosacheva, Revkov, Perkel'.

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Ethylbenzene Oxidation in the Presence of Acetic Anhydride

I. M. Nosacheva, O. A. Revkov, and A. L. Perkel'

Kuzbass State Technical University, Kemerovo, Russia

Received May 28, 2004; in final form, December 2004

Abstract—The kinetics of formation and subsequent transformation of the products of ethylbenzene oxidation in the presence of acetic anhydride at 100°C was studied by solution of the inverse kinetic problem.

Secondary hydroperoxides are the main primary molecular intermediates of liquid-phase oxidation of saturated aliphatic, alicyclic, and some alkylaromatic hydrocarbons [1–4]. These intermediates can further react with carboxylic acid anhydrides (important products of oxidative degradation of saturated hydrocarbons and their oxygen derivatives) [4, 5].

Carboxylic acid anhydrides react with hydroperoxides to form peroxy esters [4–7]. Synthesis of peroxy esters of secondary hydroperoxides and their properties are poorly studied. This is probably due to the fact that peroxy esters of secondary hydroperoxides are substantially less stable than those of primary and especially tertiary hydroperoxides and decompose even at low temperatures [6, 7].

In this work we studied the kinetics of ethylbenzene (EB) oxidation in the presence of acetic anhydride (AA). 1-Phenylethyl hydroperoxide formed in EB oxidation reacts with AA to form 1-phenylethyl peroxyacetate. In this study we examined the main relationships in formation and subsequent reaction of 1-phenylethyl peroxyacetate.

EXPERIMENTAL

Ethylbenzene (pure grade) was treated with concentrated sulfuric acid to remove oxygen-containing compounds [8] and then was distilled in an argon flow. As determined by gas–liquid chromatography, the concentration of methylphenylcarbinol and acetophenone in the resulting product was lower than 0.003 and 0.005 wt %, respectively.

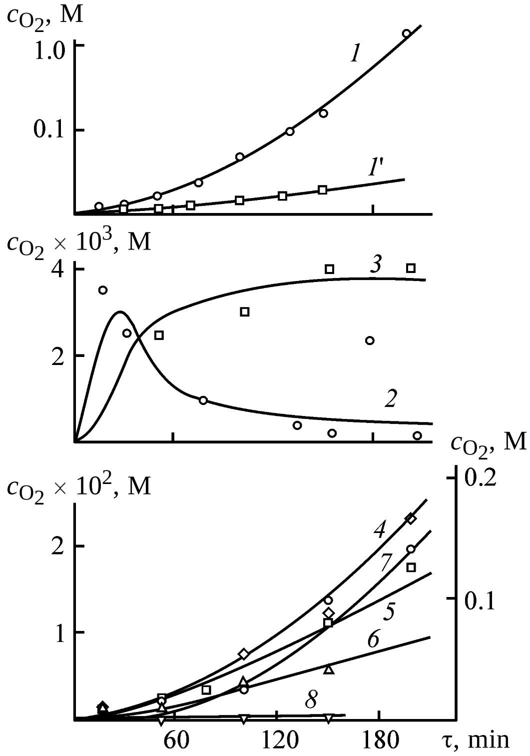
Acetic anhydride (analytically pure grade) was purified by distillation after conversion of the acetic acid impurity into methyl acetate by the reaction with diazomethane.

The total peroxide content in the EB oxidation products was determined colorimetrically after treatment of the sample with the reagent containing Fe^{2+} and *N*,*N*-dimethyl-*p*-phenylenediamine [9]. The content of 1-phenylethyl peroxyacetate (PEPA) was calculated as the difference between the content of 1-phenylethyl acetate (PEA) in the sample reduced with triphenylphosphine and in the oxidized sample. Acetic anhydride was decomposed with a methanol–pyridine mixture (1 : 1 v/v) immediately after the sampling. The content of 1-phenylethyl hydroperoxide (PEHP) was determined as the difference between the total peroxide content and the PEPA content. To determine the content of benzoic acid by GLC, it was converted into methyl benzoate by treatment with diazomethane. The GLC analysis of nonperoxide products of EB oxidation was performed at 140°C on a 2000×3-mm column; stationary phase 15% Carbowax-6000 on Chromaton N-AW-DMCS, internal reference nitrobenzene.

Ethylbenzene was oxidized in a manometric unit under the conditions of the kinetic control of the oxygen uptake.

The parameters of the kinetic equations were calculated by the least-squares procedure using the Delphi 5.5 program. A set of differential equations was solved in each step by the fourth-order Runge–Kutta method.

Peroxy esters of secondary hydroperoxides are thermally unstable and can be studied only under special conditions [6, 7] which substantially differ from the conditions of hydrocarbon oxidation. The general features of formation and subsequent transformations of peroxy esters of secondary hydroperoxides under the autooxidation conditions were studied with an example of PEPA. This compound was prepared *in situ* by reaction of AA introduced into the reaction



(*1'*) Kinetic curves of oxygen uptake in EB oxidation at 100°C in the absence of AA and kinetic curves of (*1*) total accumulation of the products of EB oxidation at 100°C in the presence of AA and accumulation of (*2*) PEHP, (*3*) PEPA, (*4*) AP, (*5*) MPC, (*6*) BAl + BAc, (*7*) PEA, and (*8*) BAc. (C_{O_2}) concentration of absorbed oxygen and the oxidation products and (τ) time. (*1–7*) Calculated curves and (*1'*, *8*) experimental curves.

mixture with PEHP formed in radical-chain oxidation of EB.

Ethylbenzene was oxidized with oxygen at 100°C in the absence of AA and in the presence of 1.1 M AA. The experimental kinetic curves of oxygen uptake (in the absence of AA), total accumulation of the EB oxidation products, and accumulation of PEHP, PEPA, methyphenylcarbinol (MPC), acetophenone (AP), PEA, benzaldehyde (BAl) + benzoic acid (BAc), and BAc are shown in the figure.

The rate of ethylbenzene oxidation to form PEHP at 100°C in the absence of AA is almost constant (see figure)

$$\text{PhCH}_2\text{Me} \xrightarrow{\text{RO}_2^*,\ \text{O}_2,\ \text{RH}} \text{PhCH(OOH)Me (PEHP)}. \quad (1)$$

Clearly, PEHP decomposition under these conditions is slow and is initiated mainly by chain generation. The rate of radical-chain oxidation of EB is described by the equation [1, 2]

$$-\text{d[RH]/d}\tau = k_p(2k_t)^{-0.5}[\text{RH}](w_i^0)^{0.5}, \quad (2)$$

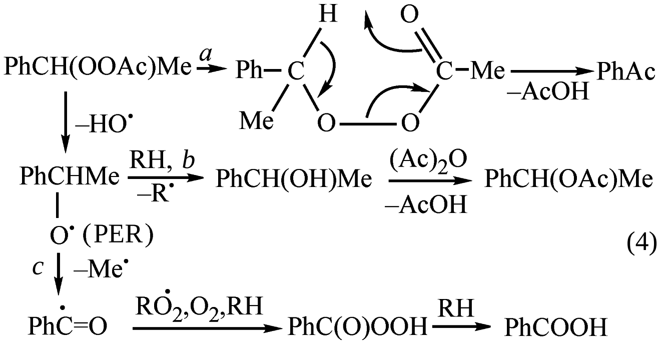
where k_p and $2k_t$ are the rate constants of chain propagation and termination, respectively; w_i^0 is the rate of initiation by chain generation.

Substitution of $k_p(2k_t)^{-0.5} = 22.2 \times 10^{-4}$ l mol$^{-0.5}$ s$^{-0.5}$ [2], the rate constant of radical-chain oxidation of EB in the absence of acetic anhydride (w_{rc} = 3.9 × 10^{-6} mol l^{-1} s^{-1}), and [RH] = 8.2 M into Eq. (2) gives w_i^0 = 4.5 × 10^{-8} mol l^{-1} s^{-1} at 100°C.

The kinetic curve of oxygen uptake in the presence of AA is more complex. In the first steps, the curve is typical of an autocatalytic process and then it becomes linear (see figure). Along with PEHP, PEPA is accumulated by acylation of PEHP with AA:

$$\text{PhCH(OOH)Me} \xrightarrow[\text{–AcOH}]{\text{(Ac)}_2\text{O}} \text{PhCH(OOAc)Me (PEPA)}. \quad (3)$$

Acceleration of EB oxidation in the presence of AA is due to increasing contribution of degenerate branching caused by homolytic decomposition of PEPA. Probably, radical decomposition of PEPA in the course of BE oxidation is faster than that of the initial PEHP [5]. The main oxidation product of EB in the presence of AA is AP. Its yield is substantially higher than that in thermal oxidation of EB at 120°C in the absence of AA [2]. We suggest that AP is formed by pericyclic transformation of PEPA [scheme (4), pathway *a*]. The relative yield of MPC in the presence of AA (see figure) is substantially lower than that in the absence of AA [2]. Probably, methylphenylcarbinol is formed by the reaction of 1-phenylethoxy radical (PER) with EB and partially reacts with AA to form PEA [scheme (4), pathway *b*]. Clearly, homolytic decomposition of PEPA yields BAl which is further oxidized to BAc [scheme (4), pathway *c*].

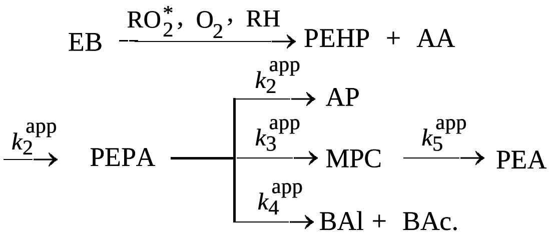


(4)

Calculated rate constants of formation and transformations of PEPA in EB oxidation in the presence of AA

i	$k_i \times 10^4$		$k_i' \times 10^2$		$(k_i'/k_i) \times 10^2$
	s^{-1}	$l\ mol^{-1}\ s^{-1}$	$l\ mol^{-1}\ s^{-1}$	$l^2\ mol^{-2}\ s^{-1}$	
0	10.00		0.19		1.90
1		9.57		16.68	174
2	32.5		0.76		2.34
3	6.13		0.22		3.59
4	2.52		0.0016		0.063
5		2.57		0.000	0.00

Thus, EB oxidation in the presence of AA can be described by the following kinetic scheme:



$$\mathrm{EB} \xrightarrow{RO_2^*,\ O_2,\ RH} \mathrm{PEHP} + \mathrm{AA}$$

$$\xrightarrow{k_2^{app}} \mathrm{PEPA} \begin{cases} \xrightarrow{k_2^{app}} \mathrm{AP} \\ \xrightarrow{k_3^{app}} \mathrm{MPC} \xrightarrow{k_5^{app}} \mathrm{PEA} \\ \xrightarrow{k_4^{app}} \mathrm{BAl} + \mathrm{BAc}. \end{cases} \quad (5)$$

Kinetics of reactions (1), (3), and (4) can be described by the following set of equations:

$$-d[EB]/d\tau = k_p(2k_t)^{-0.5}[EB](w_i^0) + k_0^{app}[PEPA]^{-0.5}, \quad (6)$$

$$d[PEHP]/d\tau = k_p(2k_t)^{-0.5}[EB](w_l^0) + k_0^{app}[PEPA]^{-0.5}$$
$$- k_1^{app}[PEPA][AA], \quad (7)$$

$$d[PEHP]/d\tau = -k_1^{app}[PEPA][AA] - (k_2^{app} + k_3^{app}$$
$$+ k_4^{app})[PEPA], \quad (8)$$

$$d[AP]/d\tau = k_2^{app}[PEPA], \quad (9)$$

$$d[MPC]/d\tau = k_3^{app}[PEPA] - k_5^{app}[MPC][AA], \quad (10)$$

$$d([BAl] + [BAc])/d\tau = k_4^{app}[PEPA], \quad (11)$$

$$d[PEA]/d\tau = k_5^{app}[MPC][AA], \quad (12)$$

$$-d[AA]/d\tau = k_1^{app}[PEHP][AA] + k_5^{app}[MPC][AA], \quad (13)$$

$$d[AA]/d\tau = k_1^{app}[PEHP][AA] + (k_2^{app} + k_3^{app} + k_4^{app})[PEPA]$$
$$+ k_5^{app}[MPC][AA], \quad (14)$$

$$\Delta[O_2] = [EB]_0 - [EB] = [PEHP] + [PEPA] + [AP]$$
$$+ [MPC] + [BAl] + [BAc] + [PEA], \quad (15)$$

where [X] is concentration of the reactants, M; $[O_2]$, amount of oxygen taken up, M; k_1^{app}–k_5^{app} are the apparent rate constants of the steps of reaction (5); and k_0^{app} is the apparent rate constant of initiation by PEPA decomposition.

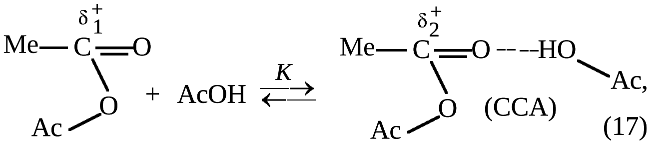
Since formation and subsequent transformations of 1-hydroxycyclohexyl peroxydodecanoate are acid-catalyzed [10, 11], we suggest that the corresponding apparent rate constants can depend on the acetic acid (AAc) concentration

$$k_i^{app} = k_i + k_i'[AAc], \quad (16)$$

where k_i is the autocatalytic constant.

The rate constants calculated by solution of the inverse kinetic problem are presented in the table, and the calculated kinetic curves are shown in the figure.

As seen from the figure, the calculated kinetic curves fit well the experimental results (the sum of squares of the deviations is 4.9×10^{-4}). Comparison of the rate constants shows that the conversion of PEPA into AP is about 75%. Although all k_i^{app}, except for k_5^{app}, depend on the AAc concentration, the autocatalytic contribution to reactions steps, as indicated by the k_i'/k_i ratio (see table), noticeably differ. The influence of AAc on acylation of PEHP with AA is the most pronounced. Clearly, the catalytic effect in this case is caused by formation of AAc–AA (CCA) complex which is more reactive than the free anhydride with respect to the nucleophilic attack of the hydroperoxide ($\delta_2^+ > \delta_1^+$):



(17)

$$(CCA) + PEHP \overset{k_2''}{\rightleftarrows} PEPA + AAc, \quad (18)$$

where k''_2 is the rate constant of reaction of PEHP with CCA and K is the equilibrium constant of reaction (17).

Taking into account reactions (17) and (18), the PEHP consumption can be described by the kinetic equation of an autocatalytic reaction

$$-\mathrm{d}[\mathrm{PEHP}]_{\mathrm{cat}}/\mathrm{d}\tau = k''_2K[\mathrm{AAc}][\mathrm{AA}][\mathrm{PEHP}]$$

$$= k'_2[\mathrm{AAc}][\mathrm{AA}][\mathrm{PEHP}]. \qquad (19)$$

Hence, $k'_2 = k''_2K$.

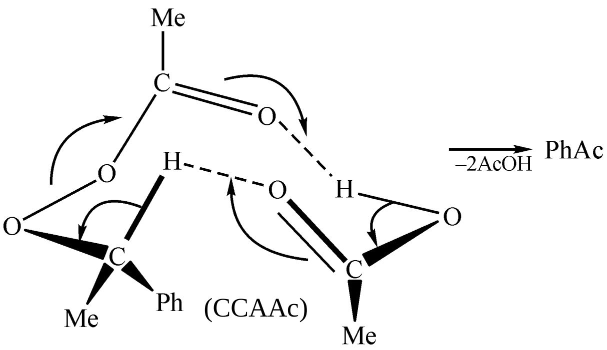
Acylation of MPC with AA should be seemingly also acid-catalyzed. However, our previous kinetic study of this reaction in chlorobenzene at 80–110°C [12] shows that AAc has no effect on this reaction. The k_5^{app} determined in this study (2.57×10^{-4} l mol^{-1} s^{-1}) is close to $k_5^{\mathrm{app}} = 2.66 \times 10^{-4}$ l mol^{-1} s^{-1} calculated from the dependence $\ln k_0 = (10.9 \pm 2.9) - (59300 \pm 8900)/RT$ [12].

The reason of this distinction is not clear. We assume that it is due to the fact that the steric hindrance in the attack of the carbon atom of the carbonyl group in CCA by the hydroxy group of MPC is stronger than that in the reaction of CCA with the hydroperoxy group of PEHP.

The influence of AAc in the step of PEPA decomposition is weaker than that in the step of its formation. The ratio k'_i/k_i (table) shows that the contribution of the autocatalytic reaction to the overall process is substantially lower [particularly, in the case of reaction (4, pathway *c*)] than in the case of decomposition of 1-hydroxycyclohexyl peroxydodecanoate (intermediate of Baeyer–Villiger oxidation of cyclohexanone with peroxylauric acid) [10, 11]. The ratio of the constants for heterolytic rearrangement of 1-hydroxycyclohexyl peroxydodecanoate (α-hydroxy peroxy ester) into lactone (18°C) is 17.3, whereas for the homolytic decomposition it is 41.8 [11]. Probably, decomposition of the peroxy ester is less acid-sensitive than that of α-hydroxy peroxy ester owing to lower probability of the decomposition by the mechanism of relay proton transfer [10, 11].

We suggest that the decomposition mechanism of PEPA in the cyclic complex with AAc (CCAAc) to form AP (20) is similar.

The apparent rate constant of initiation by homolytic decomposition of PEPA (k_0^{app}) (see table) is almost independent of the presence of acetic acid.



(20)

This constant should be related, by definition, to the apparent rate constants of PEPA decomposition into MPC and BAl by the equation

$$k_0 + k'_0[\mathrm{AAc}] = 2e(k_3 + k'_3[\mathrm{AAc}]) + (k_4 + k'_4[\mathrm{AAc}]), \qquad (21)$$

where e is the coefficient of radical escape from the solvent cage.

At [AAc] = 0.2 M, substitution of the constants in Eq. (21) gives $e = 0.57$ which is close to the known value ($e = 0.6$) for aromatic solvents [13].

Thus, carboxylic acid anhydrides substantially catalyze decomposition of secondary hydroperoxides and change the decomposition mechanism. Contrary to the previous data [7], about 25% of the peroxy ester of the secondary hydroperoxide decomposes homolytically, i.e., this compound initiates the radical-chain oxidation but to a lesser extent as compared to peroxy esters of tertiary hydroperoxides [7, 14]. Since carboxylic acid anhydrides are consumed mainly by reactions with hydroperoxides [4], formation and decomposition of peroxy esters of secondary hydroperoxides can contribute significantly to both initiation of oxidation of organic compounds and formation of carbonyl-containing products.

CONCLUSIONS

(1) Acetic anhydride substantially catalyzes radical-chain oxidation of ethylbenzene at 100°C. The primary molecular product of ethylbenzene oxidation, 1-phenylethyl hydroperoxide, decomposes via 1-phenylethyl peroxyacetate formation to give mainly acetophenone by the pericyclic mechanism.

(2) Acceleration of ethylbenzene oxidation in the presence of acetic anhydride is due to homolytic decomposition of the peroxy ester into methylphenylcarbinol and benzaldehyde.

(3) Acetic acid formed in acylation of the hydroperoxide and peroxy ester decomposition catalyzes

both peroxy ester formation and, to a lesser extent, its decomposition.

REFERENCES

1. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Reactions of Hydrocarbon Oxidation in the Liquid Phase), Moscow: Nauka, 1965.
2. Emanuel', N.M. and Gal, D., *Okislenie etilbenzola (model'naya reaktsiya)* (Ethylbenzene Oxidation (Model Reaction)), Moscow: Nauka, 1984.
3. Nazimok, V.F., Ovchinnikov, V.I., and Potekhin, V.M., *Zhidkofaznoe okislenie alkilaromaticheskikh uglevodorodov* (Liquid-Phase Oxidation of Alkylaromatic Hydrocarbons), Moscow: Khimiya, 1987.
4. Perkel', A.L., Voronina, S.G., and Freidin, B.G., *Usp. Khim.*, 1994, vol. 63, no. 9, pp. 793–809.
5. Nosacheva, I.M., Voronina, S.G., and Perkel', A.L., Abstracts of Papers, *XI Mezhdunarodnaya konferentsiya po khimii organicheskikh i elementoorganicheskikh peroksidov* (XI Int. Conf. on Chemistry of Organic and Oraganoelemental Peroxides), Moscow, June 24–26, 2003, pp. 256–257.
6. Durham, L.J., Glover, L., and Mosher, H.S., *J. Am. Chem. Soc.*, 1960, vol. 82, no. 6, pp. 1508–1509.
7. Ryukhardt, S., *Usp. Khim.*, 1968, vol. 37, no. 8, pp. 1402–1442.
8. Weissberger, A., Proskauer, E., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents. Physical Properties and Methods of Purification*, New York: Interscience, 1955.
9. Perkel', A.L., Voronina, S.G., and Perkel', R.L., *Zh. Anal. Khim.*, 1991, vol. 46, no. 11, pp. 2283–2286.
10. Shumkina, T.F., Voronina, S.G., Krutskii, D.L., and Perkel', A.L., *Zh. Prikl. Khim.*, 1995, vol. 68, no. 2, pp. 290–297.
11. Shumkina, T.F., Voronina, S.G., and Perkel', A.L., *Zh. Prikl. Khim.*, 1996, vol. 69, no. 2, pp. 287–294.
12. Perkel', A.L., Nosacheva, I.M., and Revkov, O.A., *Vestn. Kuzbassk. Gos. Tekh. Univ.*, 2004, no. 3, pp. 78–81.
13. Denisov, E.T. and Kovalev, G.I., *Okislenie i stabilizatsiya reaktivnykh topliv* (Oxidation and Stabilization of Jet Fuels), Moscow: Khimiya, 1983.
14. Antonovskii, V.L., *Organicheskie perekisnye initsiatory* (Organic Peroxy Initiators), Moscow: Khimiya, 1972.