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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Oxidation of Cumene in the Presence of High Concentrations of Ascorbic Acid

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Abstract—Initiated oxidation of cumene by oxygen in the presence of ascorbic acid was studied.

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It has been shown previously that ascorbic acid exhibits antioxidant properties in both aqueous and organic phases and, irrespective of the nature of a solvent, the duration of action of vitamin C is determined by its concentration in the system [1, 2]. The concentration range of ascorbic acid in the reaction mixture has been determined, at which its efficiency as an inhibitor of the radical-chain oxidation in the organic medium is the highest.

In this study, we continued analysis of the effect of vitamin C at its increased concentrations on the radical-chain oxidation process.

EXPERIMENTAL

As a model system was chosen the liquid-phase oxidation of cumene, initiated by 2,2-azo-di-(iso-butyronitrile) (AIBN), whose mechanism and all elementary stages are well understood [3].

Because ascorbic acid is poorly soluble in cumene, we used dimethylsulfoxide (DMSO), in which vitamin C is fully soluble in the chosen concentration range, as a reaction medium that provided homophase conditions of the process. In addition, the spectral characteristics of ascorbic acid forms produced in DMSO are known [4].

The kinetics of cumene oxidation in the presence of ascorbic acid was monitored gas-volumetrically by measuring the amount of oxygen absorbed in the course of time by solutions containing cumene, initiator (AIBN), and vitamin C. The experimental data we obtained demonstrate that a break is observed in kinetic curves of oxygen absorption by systems containing ascorbic acid in the concentration range from 1×10^{-3} to 1×10^{-2} M (Fig. 1), which enables calculation of the induction period.

The induction period duration increases with the ascorbic acid concentration, with the oxidation rate in the initial interval of time in the initial stage (inhibition stage) remains low (0.4×10^{-6} M s^{-1}) and nearly invariable. With the ascorbic acid concentration in the system being oxidized increasing further, from 1×10^{-2} to 2×10^{-2} M, the oxidation rate noticeably grows in the initial stage, whereas the increase in the induction period being not so significant as that at lower concentrations of vitamin C. The induction period duration nonlinearly depends on the ascorbic acid concentration in the range up to 2×10^{-2} M (Fig. 2).

Addition of ascorbic acid to a mixture being oxidized in amounts exceeding 2×10^{-2} M changes the shape of the curve describing the oxidation kinetics: there is no break, the oxidation rate in the initial period of time increases with the ascorbic acid concentration, and the time dependence of the oxygen volume absorbed by the system is linear during the entire oxidation period under study (Fig. 3).

It is important to note that, at ascorbic acid concentrations higher than 0.24 M, the oxidation rate of the mixture exceeds that of cumene in the absence of the inhibitor, i.e., the contribution from oxidation of ascorbic acid itself is rather noticeable. An iodometric titration of the oxidates demonstrated that a system free of ascorbic acid, studied after 30 min of oxidation, contains cumene hydroperoxide (main oxidation

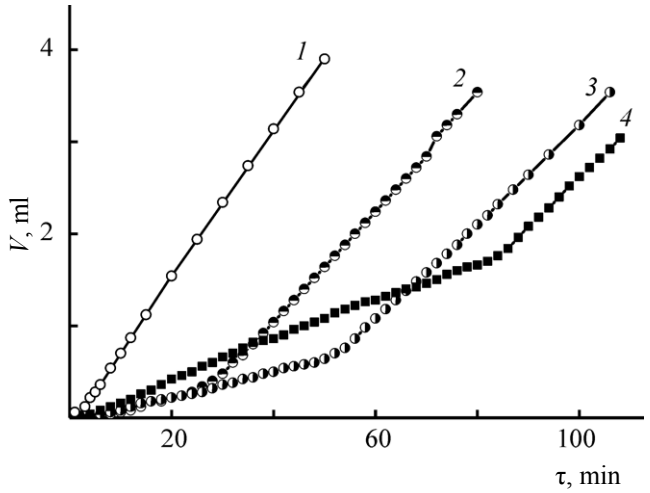

Fig. 1. Kinetics of initiated oxidation of cumene in dimethylsulfoxide in the presence of ascorbic acid. [AIBN] = 2.00×10^{-2} M, [cumene] = 3.59 M; 75°C; the same for Fig. 3. (*V*) Oxygen volume and (τ) time; the same for Fig. 3. [AA] (M): (*1*) 0, (*2*) 3.12×10^{-3}, (*3*) 9.65×10^{-3}, and (*4*) 2.33×10^{-2}.

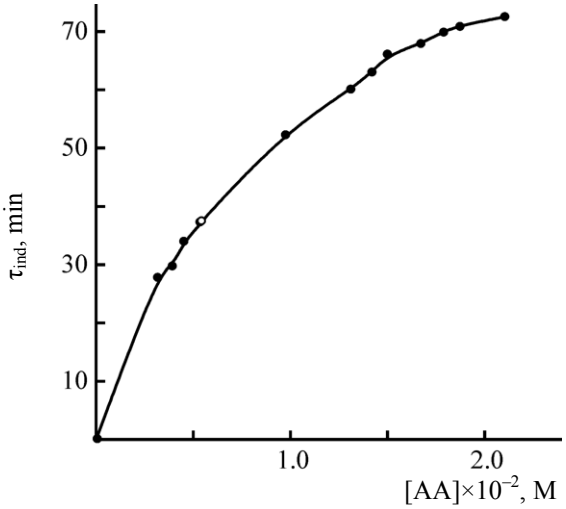

Fig. 2. Induction period duration τ_{ind} vs. the ascorbic acid concentration [AA].

product) in an amount of 0.33 M, which corresponds to 3 ml of absorbed oxygen. In a system with 0.29 M of ascorbic acid, no cumene hydroperoxide was found under comparable conditions. Thus, the absorption of oxygen by the system under study (vitamin C–cumene–DMSO–initiator) is due to oxidation of ascorbic acid itself. To confirm this fact, we replaced the substrate being oxidized, cumene, with chlorobenzene, which is inert against oxidation, with relative amounts of the rest of the reactants and the solvent remaining the same. The kinetic parameters of the system constituted by ascorbic acid, chlorobenzene, DMSO, and initiator show that the oxidation rate of ascorbic acid under these conditions is comparable with that of the vitamin C–cumene-DMSO–initiator system (see the table).

Rate of oxygen absorption by the system constituted by ascorbic acid, hydrocarbon, DMSO, and initiator [AIBN] = 2.00×10^{-2} M, 75°C

[AK]×10², M	$W_{[O]}\times10^{6}$, M s^{-1}	
	cumene	chlorobenzene
0	2.77	0
1.28	0.46	0.37
1.87	0.62	0.66
23.73	2.93	3.01

Analysis of how the oxidation rate of ascorbic acid depends on its concentration makes it possible to clearly distinguish two effects: first, introduction of vitamin C into the solvent–cumene–initiator system apparently hinders the radical-chain oxidation of cumene, and, second, addition of 1×10^{-2} to 3×10^{-1} M of ascorbic acid to the mixture being oxidized leads to a proportional increase in the overall oxidation rate of the system (Fig. 4a). Thus, the oxidation of cumene is fully suppressed upon an increase in the ascorbic acid concentration, but the oxidation of ascorbic acid itself becomes rather important.

It is impossible to study the process of oxidation of the mixture under homogeneous conditions at even higher concentrations of ascorbic acid. Introduction of ascorbic acid into a mixture being oxidized in amounts exceeding 0.4 M leads to formation of a two-phase system. This is possibly due to the hydrophilic nature of vitamin C, which separates the mixture of cumene and DMSO. It should be noted that, in this case, the process of radical-chain oxidation of cumene is decelerated. Figure 4b shows how the oxidation rate depends on the ascorbic acid concentration at concentrations exceeding 4×10^{-1} M.

The oxidation kinetics was monitored gas-volumetrically by measuring the amount of absorbed oxygen at a constant temperature of 75°C and constant partial oxygen pressure of 760 mm Hg on the installation described in [5]. The process was studied

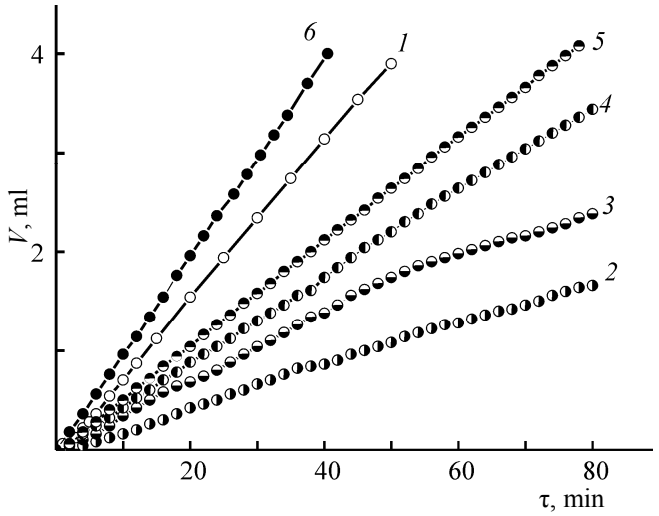

Fig. 3. Kinetics of initiated oxidation of cumene in dimethylsulfoxide in the presence of ascorbic acid. [AA] (M): (*1*) 0, (*2*) 3.38×10^{-2}, (*3*) 6.62×10^{-2}, (*4*) 8.77×10^{-2}, (*5*) 1.23×10^{-1}, and (*6*) 2.89×10^{-1}.

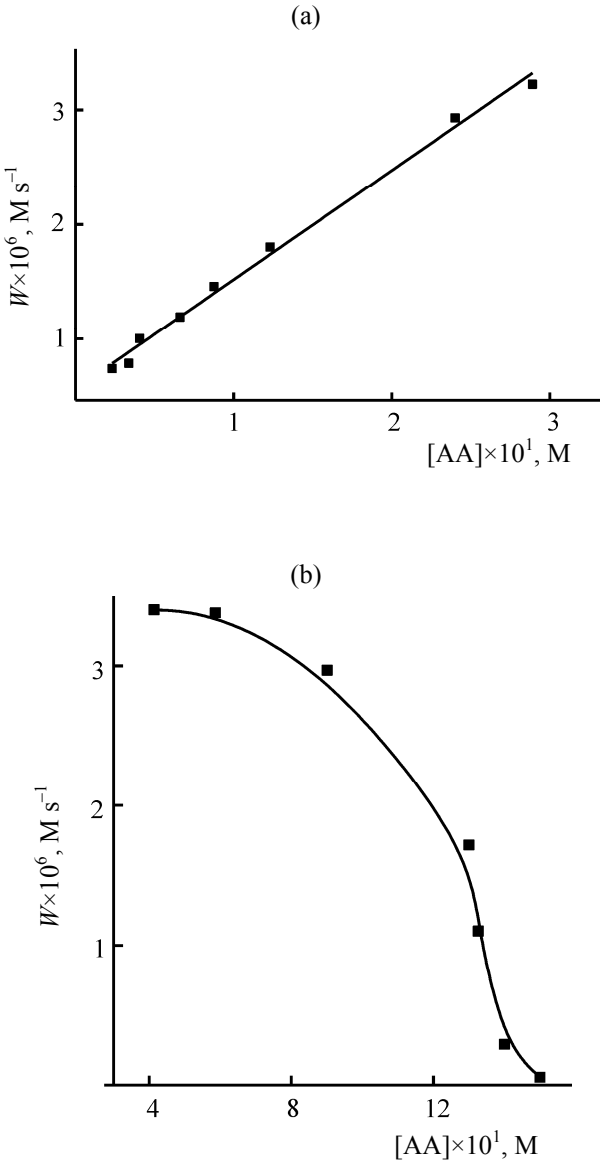

Fig. 4. Oxidation rate *W* of the system vs. the ascorbic acid concentration [AA] in the ranges (a) from 1×10^{-2} to 3×10^{-1} M and (b) from 4×10^{-1} to 12×10^{-1} M.

under homogeneous conditions in the kinetic region, in which the reaction rate ceases to be dependent on the agitation rate. We graphically determined the induction period duration from the resulting kinetic curves by extrapolating their linear portions until their intersection and then dropping a perpendicular to the abscissa axis. The induction period duration was found as the length of the segment cut off on the time axis. Hydroperoxide derivatives were determined by the standard iodometric procedure [6].

We used the following reagents: AIBN, cumene, chlorobenzene, dimethylsulfoxide, and acetonitrile purified as described in [7]; twice distilled water; and ascorbic acid [FS (Pharmacopoeic Article) 42-2668–89] with a specific rotation of $+20.9\pm0.4$. The concentrations of cumene and AIBN in the systems under study were 3.59 and 2.00×10^{-2} M, respectively.

CONCLUSIONS

(1) In initiated liquid-phase oxidation of cumene, ascorbic acid behaves as a typical inhibitor when present at low concentrations (on the order of 10^{-3} M). At concentrations exceeding 1×10^{-2} M, there is no induction period and the initial rate of the oxidation process increases with the concentration of vitamin C.

(2) In initiated oxidation of cumene in the presence of ascorbic acid in amounts exceeding 1×10^{-1} M, there is no cumene hydroxide in the oxidation products and the absorption of oxygen is due to the oxidation of ascorbic acid itself.

(3) Upon introduction of ascorbic acid into a system being oxidized in amounts exceeding 4×10^{-1} M, the oxidation process becomes slower with increasing concentration of vitamin C, which is due to transition of the system to the heterogeneous region.

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