ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 1, pp. 98−101. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © O.V. Smirnova, I.V. Efimova, I.A. Opeida, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 1, pp. 99−102.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Behavior of Ascorbic Acid in Hetero- and Homophase Chain-Radical Oxidation Processes

O. V. Smirnova, I. V. Efimova, and I. A. Opeida

Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk, Ukraine

Received July 1, 2008

Abstract—Initiated hetorophase oxidation of cumene with oxygen was examined in the presence of ascorbic acid in a wide concentration range.

DOI: 10.1134/S1070427209010182

Ascorbic acid is a unique polyfunctional compound capable of reversible oxidation and reduction that makes it suitable as participant of the most important energy-related processes in living cells [1, 2], a recognized antioxidant [3], and an active antidote of free-radical processes intensified in pathological situations. Ascorbic acid undoubtedly participates in growth, as well as vegetative and reproductive differentiation, in water exchange processes, regulation of enzymatic activity, stimulation of metabolic reactions associated with exchange of nucleic acids and protein synthesis, and protective responses of plants [4]. It is believed that ascorbic acid performs its protective function in the aqueous phase on the membrane surface, by contrast to lipophilic compounds like α-tocopherol or Vitamin E.

Ascorbic acid is also known [5] as a medium-strength inhibitor of oxidation of food fats, as well as an efficient synergist. However, its complexes with transition metals accelerate oxidation of the fat phase of foodstuffs, since transition metals catalyze autooxidation of ascorbic acid [6, 7]. As known [8], metals are the major pro-oxidants increasing the redox potential and accelerating oxidation of lipids, and ascorbic acid in low concentrations also exhibits pro-oxidant properties. Nonenzymatic oxidation of ascorbic acid is catalyzed by hydroxy ions and bi- and trivalent metals, especially by copper [9]. In a complex biologic system Vitamin C is determined as the sum of interconverting reduced and oxidized forms of ascorbic acid. In this context, of much interest is the behavior of ascorbic acid as inhibitor of chain-radical oxidation in organic media.

EXPERIMENTAL

As a model system we chose initiated liquid-phase oxidation of cumene, the mechanism of whose oxidation and all the elementary stages are well understood [10].

The cumene oxidation initiated with azodiisobutyronitrile (AIBN) was examined under varied concentrations of ascorbic acid in different media at 75°C. As the reaction medium for homophase oxidation we used aprotic solvents dimethylsulfoxide (DMSO) and acetonitrile, where the spectral characteristics of the resulting ascorbic acid species were examined the most extensively. Heterophase oxidation was examined in a 2:1:1 cumene–acetonitrile–water mixture. In this mixture, the organic-to-aqueous phase ratio was 3:1, and in a 1:1 cumene–water mixture, 1:1.

We examined both homo- and heterogeneous processes in the kinetic region, where the reaction rate is independent of the stirring rate. Figure 1 shows the plots of substrate oxidation rate vs. stirring rate. We found that, at stirring rates above 4 rps for the system in the reactor, the reaction rate is virtually independent of the stirring rate. All the subsequent experiments were run at the stirring rate 5 rps.

Figure 2 shows the kinetic curves describing homo- and heterogeneous oxidation of cumene with oxygen in the presence of identical amounts of ascorbic acid [AA] = 5.00×10^{-3} M. In all cases we observed an inhibition effect.

As known, a conjugate interconverting redox pair, ascorbic acid and dehydroascorbic acid, inhibit free-radical processes.

In heterophase oxidation of cumene, with water and acetonitrile–water mixture as solvent, an increase in the ascorbic acid concentration caused both the process rate and the induction period to decrease relative to those for homophase oxidation in acetonitrile and dimethylsulfoxide.

Upon introduction of ascorbic acid into the system under homo- and heterophase conditions, an increase in the ascorbic acid concentration caused both the initial oxidation rate and that after completion of the induction period to decrease (see table).

We examined chain-radical oxidation of cumene in aprotic polar media under varied inhibitor concentration. The medium did not substantially affect the oxidation rate under homophase conditions with acetonitrile and DMSO as solvents. However, a change to a different solvent markedly affected the induction period. With increasing ascorbic acid concentration in DMSO the induction period increased, though differently from the case of acetonitrile. The plot of the induction period vs. ascorbic acid concentration in DMSO and acetonitrile is represented by a curve reaching saturation (Fig. 3).

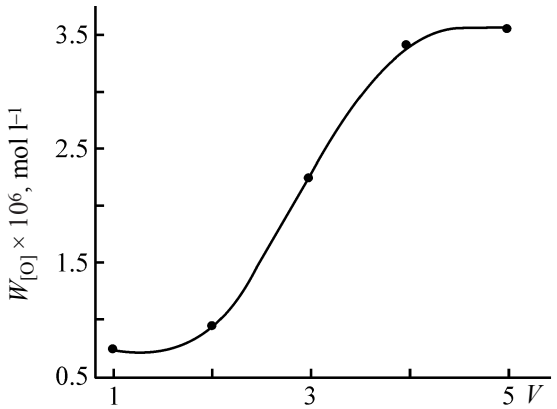

Fig. 1. Rate of initiated oxidation of cumene W[O], mol l^{-1}s^{-1}, in the heterophase system vs. stirring rate. Organic phase: aqueous phase=1:1.

The solubility of ascorbic acid in acetonitrile was experimentally estimated at 1.02×10^{-2} M, and in cumene ascorbic acid is virtually insoluble. A nonlinear variation of the induction period with the ascorbic acid concentration in the system with acetonitrile can be due to achievement of the limiting solubility of ascorbic acid in it.

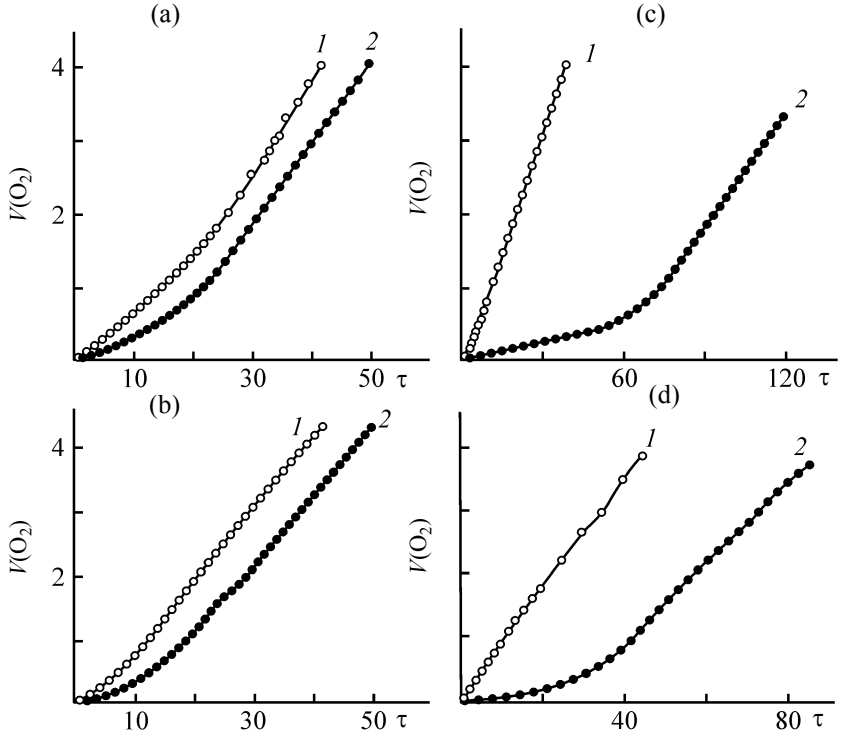

Fig. 2. Kinetic curves of initiated oxidation of cumene $V(O_2)$, ml, under homo- and heterogeneous conditions in the presence of ascorbic acid. [AIBN] = 2.00×10^{-2} M, 75°C; the same for Figs. 3, 4. (τ) time, min; the same for Fig. 4. (*1*) Without and (*2*) with ascorbic acid (5.00×10^{-3} M). (a, b) Heterogeneous conditions: (a) cumene–water (1:1) and (b) cumene–acetonitrile–water (2:1:1), and (c, d) homogeneous conditions: (c) cumene–acetonitrile (1:1) and (d) cumene–dimethylsulfoxide (1:1).

Induction period and oxidation rate after completion of the induction period for homo- and heterophase initiated oxidation of cumene [AIBN] = 2.00 × 10–2 M, [AA] = 5.50 ×10–3 M, 75°C

System	$W_{[O]} \times 10^6$, mol l^{-1} s^{-1}	τ, min
Heterophase process		
Water	1.52*	0*
	1.75	10
Acetonitrile:water = 1:1	1.88*	0*
	1.78	8
Homophase process		
Acetonitrile	2.21*	0*
	2.00	56
Dimethylsulfoxide	2.76*	0*
	2.16	33

* For processes run without ascorbic acid.

Within the concentration range examined (10–3 – 10–1 M) ascorbic acid is completely dissolved in DMSO. However, the induction period still varies nonlinearly with the ascorbic acid concentration in the system with DMSO. At the same time, the induction period is independent of ascorbic acid concentrations above 10–2 M. At ascorbic acid concentrations in DMSO within 10–2 –10–1 M the kinetic curve of oxidation exhibits a change in its run (Fig. 4). No inhibition effect in observed in the initial stage of the process, though at such inhibitor concentration there should still be a long induction period.

The above-said suggests that, whatever the solvent, the antioxidant properties of ascorbic acid are determined

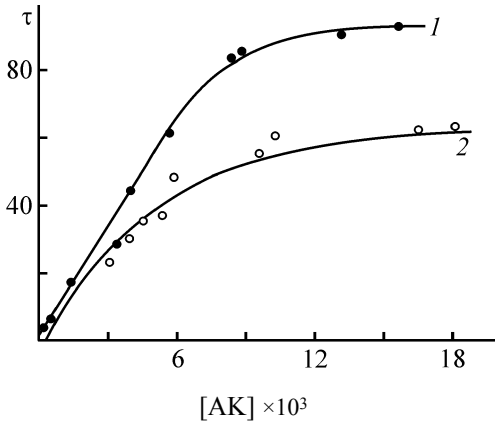

Fig. 3. Induction period τ, min, vs. ascorbic acid concentration [AA], M, for initiated oxidation of cumene in aprotic medium: (*1*) acetonitrile and (*2*) dimethylsulfoxide.

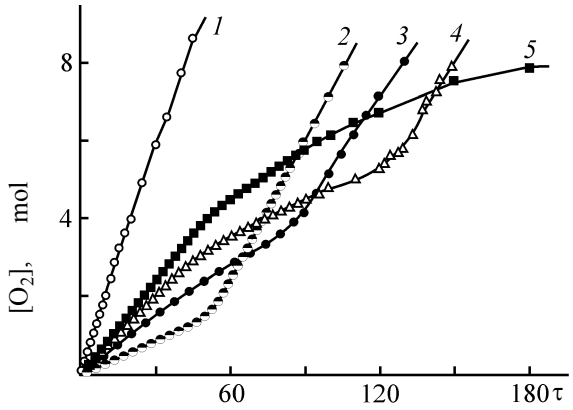

Fig. 4. Kinetic curves of initiated oxidation of cumene [O_2], M, in dimethylsulfoxide in the presence of varied concentrations of ascorbic acid: (*1*) without and (*2*–*5*) with inhibitor in concentration of, M: (*2*) 0.96 × 10–2, (*3*) 2.55 × 10–2, (*4*) 4.06 × 10–2, and (*5*) 6.68 ×10–2.

by its concentration in the system. The cumene oxidation process is inhibited most efficiently at ascorbic acid (inhibitor) concentrations of up to 10–2 M.

We followed the oxidation kinetics by gas volumetric method via measuring the oxygen uptake at a constant temperature of 75°C and constant partial oxygen pressure of 760 mm Hg on a setup described previously [11]. Azodiisobutyronitrile, cumene, dimethylsulfoxide, and acetonitrile were purified by the procedure described in [12]; we used double-distilled water and ascorbic acid according to FS (Federal Standard) 42-2668-89. Also, we determined the quality indicators of ascorbic acid; the specific rotation was estimated at +20.9 ± 0.4.

CONCLUSIONS

(1) Examination of azodiisobutyronitrile-initiated heterophase oxidation of cumene with oxygen in the presence of ascorbic acid showed that the oxidation process is weakly affected by the composition of the heterogeneous system.

(2) The plots of the induction period vs. ascorbic acid concentration in the system with dimethylsulfoxide and acetonitrile suggest that this is a process attaining saturation.

(3) The optimal range of ascorbic acid concentrations in the reaction mixture was elucidated where it exhibits the strongest inhibition effect in chain-radical oxidation of hydrocarbons in organic media.

REFERENCES

1. Ming-Ching, Yu C. and Brand, J.J., *Biochim. Biophys. Acta*, 1980, vol. 591, no. 2, pp. 483–487.

2. Gogotov, A.F., Zav'yalova, A.A., and Levchuk, A.A., *Khim. Rast. Syr'ya*, 2006, no. 3, pp. 49–52.
3. Bradshaw, M.P., Cheyner, V., Scollary, G.R., and Prenzler, P.D., *J. Agr. Food Chem*., 2003, vol. 51, pp. 4126–4132.
4. Chupakhina, G.N., *Sistema askorbinovoi kisloty rastenii* (The Ascorbic Acid System of Plants), Kaliningrad: Kaliningrad. Univ., 1997.
5. Ratushnyi, A.S., Khlebnikov, V.I., and Baranov, B.A., *Tekhnologiya produktsii obshchestvennogo pitaniya* (Technology of Public Catering Products), Moscow: Mir, 2003, vol. 1.
6. Borisenkova, S.A., Girenko, E.G., and Kaliya, O.L., *Ross. Khim. Zh*., 1999, vol. 42, no. 5, pp. 111–115.
7. Mel'nikova, N.B. and Ioffe, I.D., *Khim. Rast. Syr'ya*, 2002, no. 2, pp. 93–103.
8. Bogatova, O.V. and Dogareva, N.G., *Khimiya i fizika moloka* (Milk Chemistry and Physics), Orenburg: Orenburg Gos. Univ., 2004.
9. Davies, M.B., Austin, J., and Partridge, D.A., *Vitamin C: Its Chemistry and Biochemistry*, Royal Society of Chemistry, 1991.
10. Opeida, I.A. and Kucher, R.V., *Ukr. Khim. Zh*., 1970, vol. 36, p. 1040.
11. Emanuel', N.M., Zaikov, G.E., and Maizus, Z.K., *Rol' sredy v radikal'no-tsepnykh reaktsiyakh okisleniya organicheskikh soedinenii* (Role of Medium in Chain-Radical Oxidation of Organic Compounds), Moscow: Nauka, 1973.
12. Armarego, Wilfred, L.F. and Chai, Christina, L.L.., *Purification of Laboratory Chemicals*, *5E*, Elsevier Sci., 2003, ISBN-10: 0-7506-7571-3.