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Kinetics and Products of Acetophenone Oxidation with Ozone–Air Mixture in Acetic Acid Medium

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Abstract—Various factors affecting kinetics of acetophenone oxidation with ozone in acetic acid medium at 15–40°C have been examined. Scheme of the acetophenone oxidation with ozone via the radical mechanism has been proposed.

Keywords: acetophenone, ozone, oxidation, acetic acid, mechanism, kinetics

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Acetophenone is a stable intermediate of ozone reaction with ethylbenzene; further oxidation converts acetophenone into benzoic acid. However, details of kinetics and mechanism of these transformations have remained unclear so far. In this study we examined various factors affecting kinetics of ozone reaction with acetophenone in acetic acid medium at 15–40°C.

The preliminary studies revealed that oxidation of acetophenone with air oxygen at 15–40°C was very slow, only traces of benzoic acid were detected after passing air through acetophenone solution in acetic acid during 15 h at 15°C.

Using air–ozone mixture instead of air accelerated the reaction; however, its rate of 1.6×10^{-5} mol L^{-1} s^{-1} remained significantly lower than those of oxidation of ethylbenzene (8.3×10^{-5} mol L^{-1} s^{-1}) and α-hydroxyethylbenzene (4.4×10^{-4} mol L^{-1} s^{-1}) under similar conditions [1]. The relatively low oxidation rate was primarily responsible for the accumulation of significant amounts (34% [1]) of acetophenone in the ethylbenzene oxidation products. The major product of ozone reaction with acetophenone at 15°C was benzoic acid (96.2%); the aliphatic peroxides (3.2%) were formed as well via destructive ozonolysis of the benzene ring along with carbon dioxide (Fig. 1).

Variation of ozone concentration in the mixture led to the proportional change in the reaction rate, the selectivity of the acetophenone oxidation at the side chain not changing noticeably (Table 1). Replacement of the ozone–air mixture with the ozone-oxygen one practically did not affect the oxidation process.

Similarly, increasing the reaction temperature from 15 to 40°C accelerated the process by more than three times, whereas the oxidation selectivity remained constant (Table 2).

The acetophenone oxidation developed without any induction period (Fig. 1). The initial rate of acetophenone consumption was of 1.6×10^{-5} mol L^{-1} s^{-1}, that of ozone being of 1.7×10^{-5} mol L^{-1} s^{-1} (the latter value was calculated from the difference of ozone concentrations at the reactor inlet and outlet). Hence, $r_{O2}/r_{ArH} = 1.06$, and kinetics of ozone reaction with acetophenone at temperature up to 15°C was described by the second-order equation: $r_{O2} = k_{app}[O_3]_0[ArC(O)CH_3]_0$ with r_{O2} being the initial ozone consumption rate and k_{app} being the apparent reaction rate constant, L mol^{-1} s^{-1}. Similar conclusion on the reaction rate order with respect to the reactants was made from analysis of the initial rate of acetophenone oxidation as function of the reactants concentration (Fig. 2). The stoichiometric coefficient for ozone at 15°C was of 2.04 over a wide range of the $[O_3]_0/[ArC(O)CH_3]_0$ ratios. The apparent bimolecular rate constant for ozone consumption was of 0.040 ± 0.003 L mol^{-1} s^{-1}.

Heating above 15°C led to deviation of the kinetics from the first-order with respect to the reactants. The

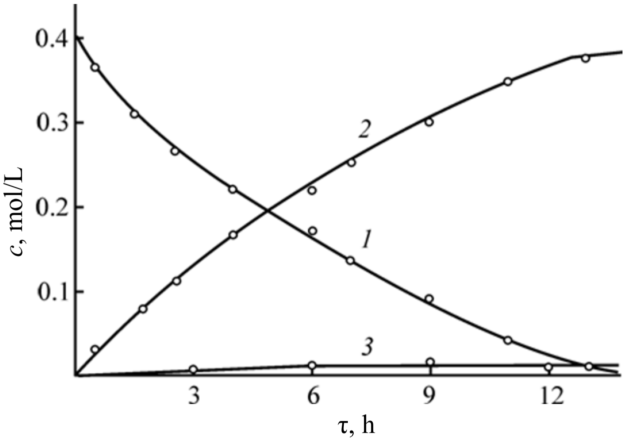


Fig. 1. Kinetics of acetophenone oxidation with ozone in acetic acid at 15°C. $[ArC(O)CH_3]_0=0.4$ mol/L, $[O_3]_0 = 5.2 \times 10^{-4}$ mol/L, mixture volume 0.01 L, and ozone–air mixture feeding rate 30 L h^{-1}. Curves *1*–*3* describe the concentrations of acetophenone, benzoic acid, and aliphatic peroxides, respectively.

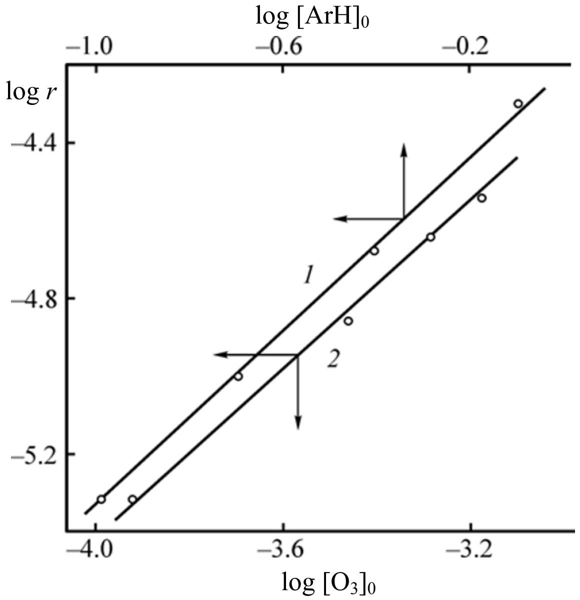


Fig. 2. Rate of acetophenone oxidation with ozone as function of the substrate (*1*) and ozone (*2*) concentrations at 15°C. $[ArC(O)CH_3]_0 = 0.4$ mol/L and $[O_3]_0 = 5.2 \times 10^{-4}$ mol/L.

kinetic data shown in Fig. 3 confirmed that the linear dependence (1) was held at a constant temperature within the 15–40°C range, and the experimental expression for the ozone consumption rate corresponded to Eq. (2).

$$k_{app} = k' + k''\cdot\sqrt{[O_3]_0/[ArC(O)CH_3]_0}, \quad (1)$$

$$r_{O2} = k'[O_3]_0[ArC(O)CH_3]_0 + k''[O_3]_0^{1.5}[ArC(O)CH_3]_0^{0.5}. \quad (2)$$

Here, k 'and k'' are temperature-dependent empirical parameters: $k' = 1.4 \times 10^2\exp(-19500/RT)$ and $k'' = 6.2 \times 10^{12}\exp(-74000/RT)$, L mol^{-1} s^{-1}.

Table 1. Effect of the ozone concentration on the selectivity of acetophenone oxidation at the side chain *S* with the ozone-air mixture at 15°C[a]

$[O_3]_0 \times 10^{-4}$, mol/L	τ, h	$r_0 \times 10^5$, mol L^{-1} s^{-1}	*S*, %
1.2	10.4	0.45	96.1
3.5	6.2	0.91	95.9
5.2	4.6	1.60	96.2
6.7	2.1	2.96	96.0
7.7	1.6	5.30	95.8

[a] $[ArC(O)CH_3]_0 = 0.4$ mol/L; ozone-air mixture feed rate 30 L h^{-1}, and mixture volume 0.01 L; (τ) is time of acetophenone concentration half-decrease and r_0 is the initial oxidation rate.

The first term of Eq. (2) is a typical expression for the second-order reaction rate (3) describing the primary reaction of ozone with acetophenone via a non-chain mechanism both at the α-carbon atom of the side chain and at the benzene ring.

$$r'_{O2} = k'[O_3]_0[ArC(O)CH_3]_0. \quad (3)$$

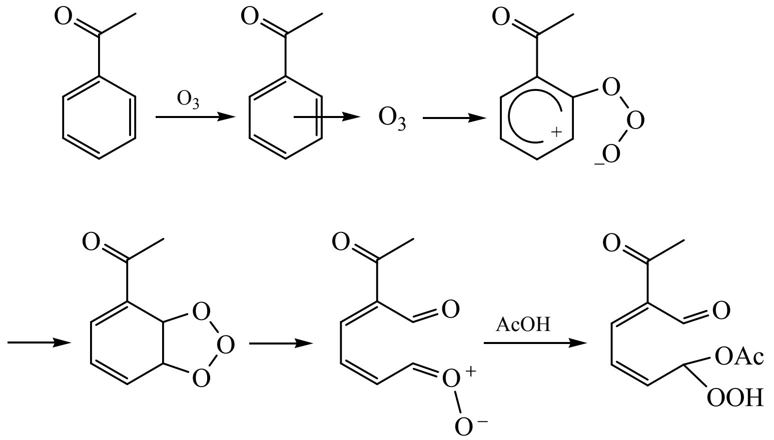
Interpretation of the above-described kinetic data according to the existing views on ketones oxidation [2, 3] and ozone reactions with aromatic compounds [4, 5] suggested the two possible schemes of non-chain oxidation of acetophenone: at the benzene ring via the Criegee mechanism (Scheme 1) [5] and at the side chain α-carbon atom via the radical mechanism (Scheme 2) [2–4].

Scheme 1 accounted for the experimentally determined number of the hydroperoxide groups in the products of the benzene ring ozonolysis (one group per

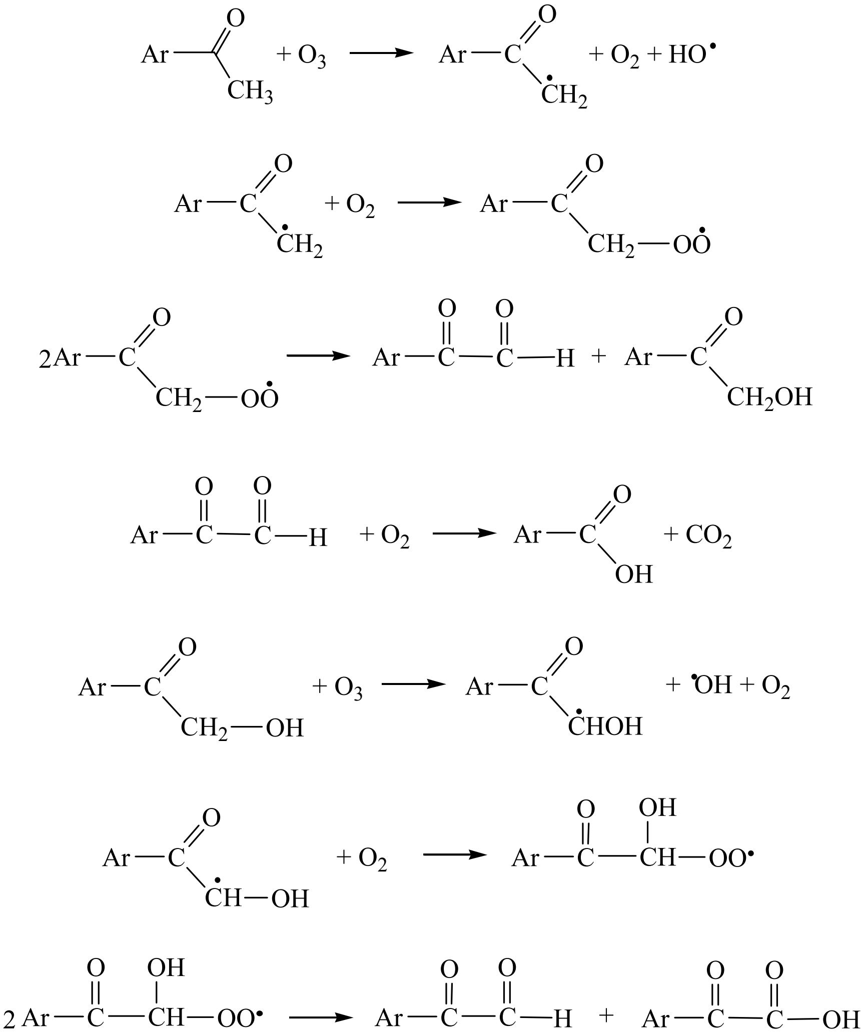
Table 2. Effect of temperature on acetophenone oxidation with ozone–air mixture in acetic acid

T, °C	$r_0 \times 10^5$, mol L^{-1} s^{-1}	*S*, %
15	1.6	96.2
20	2.2	95.9
30	3.3	96.1
40	5.5	96.0

Scheme 1.



Scheme 2.



$$\mathrm{Ar{-}C({=}O){-}CH_3} + \mathrm{O_3} \longrightarrow \mathrm{Ar{-}C({=}O){-}\dot{C}H_2} + \mathrm{O_2} + \mathrm{HO^{\bullet}} \tag{4}$$

$$\mathrm{Ar{-}C({=}O){-}\dot{C}H_2} + \mathrm{O_2} \longrightarrow \mathrm{Ar{-}C({=}O){-}CH_2{-}O\dot{O}} \tag{5}$$

$$\mathrm{2Ar{-}C({=}O){-}CH_2{-}O\dot{O}} \longrightarrow \mathrm{Ar{-}C({=}O){-}C({=}O){-}H} + \mathrm{Ar{-}C({=}O){-}CH_2OH} \tag{6}$$

$$\mathrm{Ar{-}C({=}O){-}C({=}O){-}H} + \mathrm{O_2} \longrightarrow \mathrm{Ar{-}C({=}O){-}OH} + \mathrm{CO_2} \tag{7}$$

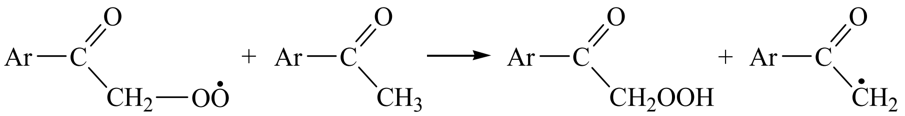
$$\mathrm{Ar{-}C({=}O){-}CH_2{-}OH} + \mathrm{O_3} \longrightarrow \mathrm{Ar{-}C({=}O){-}\dot{C}HOH} + \mathrm{{}^{\bullet}OH} + \mathrm{O_2} \tag{8}$$

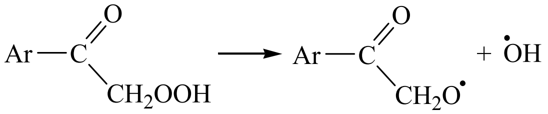
$$\mathrm{Ar{-}C({=}O){-}\dot{C}H{-}OH} + \mathrm{O_2} \longrightarrow \mathrm{Ar{-}C({=}O){-}CH(OH){-}OO^{\bullet}} \tag{9}$$

$$\mathrm{2\,Ar{-}C({=}O){-}CH(OH){-}OO^{\bullet}} \longrightarrow \mathrm{Ar{-}C({=}O){-}C({=}O){-}H} + \mathrm{Ar{-}C({=}O){-}C({=}O){-}OH} \tag{10}$$

molecule), and Scheme 2 was developed in view of the ozone consumption [two mol of ozone per a mol of acetophenone via reactions (4) and (8)].

Scheme 2 assumed that acetophenone oxidation proceeded via a radical non-chain mechanism under the experimental conditions. The chain oxidation of the ketone via reactions (11), (12) did not occur according to the experimental data: acetophenone hydroperoxide was not formed, and the oxidation completely stopped when the ozone supply was terminated.


(11)


(12)

The non-chain reaction mechanism was further confirmed by the calculations suggesting that the reaction between the peroxide radicals formed in the system was faster than that of the radical with acetophenone. For example, assuming that $r_4 = r_6$ according to the Bodenshtein–Semenov stationary concentration principle [2], at 15°C with $[ArC(O)CH_3]_0 = 0.4$ mol/L, $[O_3]_0 = 5.2 \times 10^{-4}$ mol/L, $k_4 = 0.04$, $k_6 \approx 1.7 \times 10^6$, and $k_{11} \approx 0.02$ L mol $^{-1}$ s^{-1} (the average values for the known ketones were taken to estimate k_6 and k_{11} [5]), the calculation gave $r_6 \approx 8.3 \times 10^{-6}$ mol L^{-1} s^{-1}and $r_{11} \approx 1.8 \times 10^{-8}$ mol L^{-1} s^{-1}, i.e., $r_{11}:r_6 << 1$.

The second term in Eq. (2) describes the rate of radical chain process of ozone consumption (13).

$$r'' = k''[O_3]_0^{1.5}[ArC(O)CH_3]_0^{0.5}. \qquad (13)$$

Ozone consumption via the chain mechanism was also indicated by the dependence of the stoichiometric coefficient for ozone (n) on the reaction temperature: $n = 2.04$ (15°C), $n = 2.6$ (40°C), and $n = 3$ (60°C).

A possible route of ozone consumption via a chain mechanism can be described by Eqs. (14), (15) [4].

$$ROO^{\bullet} + O_3 \rightarrow RO^{\bullet} + 2O_2, \qquad (14)$$

$$RO^{\bullet} + O_3 \rightarrow RO_2^{\bullet} + O_2, \qquad (15)$$

R stands for any peroxide radical in the equations above.

To conclude, it was found that acetophenone oxidation with ozone–air mixture in glacial acetic acid at 15–40°C proceeded predominantly at the side chain to form benzoic acid (96.2%); 3.2% of acetophenone underwent destructive ozonolysis of the aromatic ring. A possible scheme of non-chain radical ozonation of acetophenone has been proposed, with initiation of the oxidation at the side chain proceeding via a reaction with ozone. At higher temperature, ozone consumption via a chain mechanism accompanied the radical non-chain oxidation of acetophenone.

EXPERIMENTAL

Acetophenone ("chemical pure" grade) was used as received; glacial acetic acid ("chemical pure" grade) was purified via repeated fractional freezing and distillation at 118.5°C.

Acetophenone concentration in solution was determined by gas-liquid chromatography using a chromatograph equipped with a flame ionization detector and a 1 m × 3.5 mm column packed with Inerton Super carrier coated with FFAP stationary phase (5 wt % of the carrier). Other conditions were as follows: thermostat heating from 115 to 175°C within 10 min; 1.8 L/h of nitrogen, 1.8 L/h of hydrogen, and 18 L/h of air. 4-Nitrochlorobenzene was used as internal reference. Concentrations of the peroxide products and the carboxylic acids were determined by titration (iodometric and neutralization, respectively).

Oxidation of acetophenone was carried out in a temperature-controlled (15–40°C) glass column with a

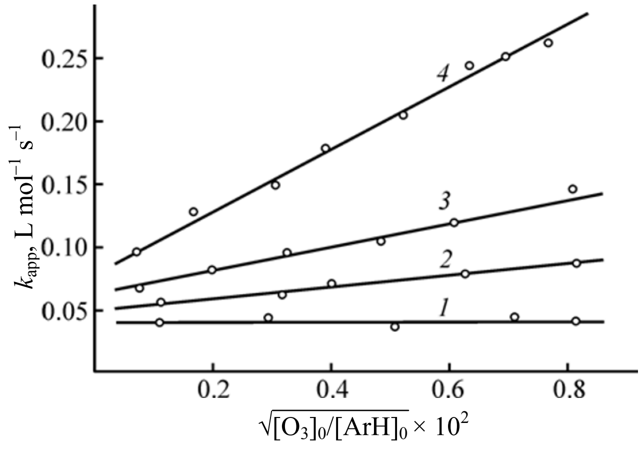


Fig. 3. Apparent rate constant of ozone reaction with acetophenone as function of the reactants concentration at (*1*) 15, (*2*) 20, (*3*) 30, and (*4*) 40°C.

porous glass separator for dispersing the ozone–air mixture, in the kinetic regime. The column was charged with 10 mL of glacial acetic acid and 0.4 mol/L of acetophenone, and then the ozone–air mixture was fed at 30 L h^{-1}. The ozone-air mixtures with ozone concentration of 10^{-4}–10^{-3} mol/L were prepared using a laboratory ozone generator described in [6]. Ozone concentrations in the gas phase at the column inlet and outlet were determined by spectrophotometry at 254–290 nm. The ozonation reaction rate constant was determined via the procedure described in [6] using an ideal-mixing reactor equipped with a constant-temperature jacket. The gas and the liquid phases were mixed in the reactor by shaking. Under those conditions, the oxidation proceeded in the kinetic regime.

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