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The Role of Oxygen in the Reaction of Ferrocene with Benzoyl Peroxide

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Abstract—Participation of molecular oxygen in the reaction of ferrocene with benzoyl peroxide in various solvents is demonstrated. The stoichiometry of the reaction ferrocene : oxygen is determined at 2 : 1. Based on NMR, IR spectroscopy, iodometry, and elemental analysis of the product the formation of [μ-(peroxy-*O*:*O*')]-diferrocenium benzoate is suggested.

Keywords: ferrocene, oxidation, peroxides, kinetics
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Ferrocene and its derivatives are well studied and find wide application in organic synthesis, material science, biology and medicine [1–5]. Ferrocene–benzoyl peroxide system is often used as an initiator of vinyl monomers polymerization in an inert atmosphere [6] and in the presence of oxygen [7].

The formation of ferrocenium radical-cation was detected at the oxidation of ferrocene with various oxidants; some investigators note that it was unstable in air [8–11]. When studying the properties of ferrocenium radical-cation under the conditions of its electrochemical generation in polar solvents saturated with oxygen, the possibility of formation of μ-peroxy dimeric iron complex as an unstable intermediate was discussed [12]. Earlier the formation of such intermediates (Fe–OO–Fe) was suggested for auto-oxidation of iron-containing porphyrins [13].

In the present paper we have studied the reaction of the *in situ* generated ferrocenium radical-cation with molecular oxygen and determined its stoichiometry.

Scheme 1.

$$Cp_2Fe + \left(Ph-\underset{\underset{O}{\|}}{C}-O\right)_2 \xrightarrow[-PhC(O)O^{\bullet}]{} [Cp_2Fe^{\bullet+}]PhCO_2^-,$$

$$2[Cp_2Fe^{\bullet+}]PhCO_2^- + {}^3O_2 \longrightarrow [Cp_2Fe{-}OO{-}FeCp_2](PhCO_2)_2.$$

Ferrocenium radical-cation was generated *in situ* in various solvents (EtOH, MeCN, *p*-xylene, and ethylbenzene) by the reaction of ferrocene (Cp_2Fe) with benzoyl peroxide (Scheme 1). The formation and consumption of the ferrocenium radical-cation was monitored spectrophotometrically in argon and oxygen atmosphere. In the inert atmosphere the formation of the ferrocenium radical-cation is the only process, while in the presence of oxygen its consumption is also observed (Fig. 1).

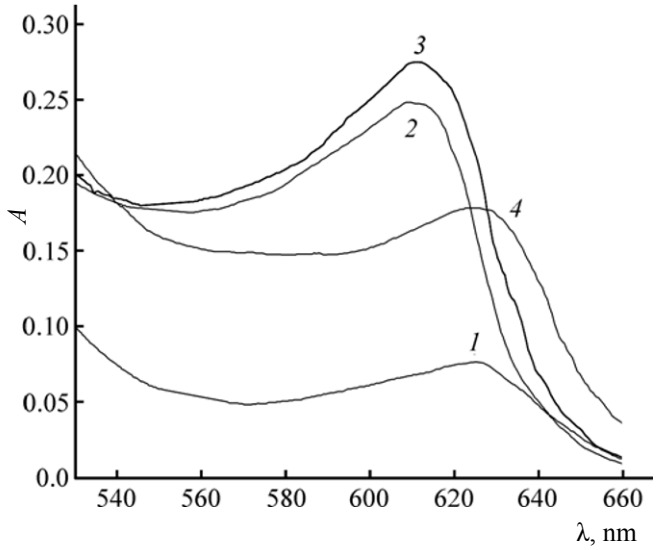

Fig. 1. Electron absorption spectrum of the system ferrocene–benzoyl peroxide in acetonitrile at 285 K: (*1*) 4 min, (*2*) 7 min, (*3*) 22 min, and (*4*) 32 min, $[Cp_2Fe]_0$= 5.00×10^{-3} mol/L, $[BP]_0 = 1.25 \times 10^{-3}$ mol/L.

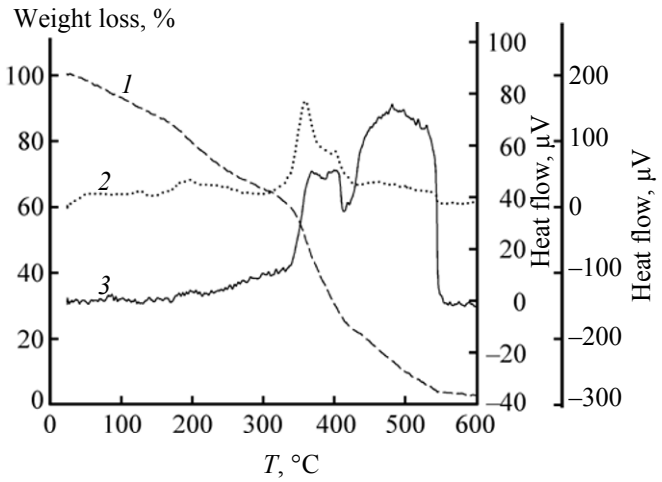

Fig. 2. Derivatogram of the reaction product of ferrocene with benzoyl peroxide in isooctane in oxygen atmosphere: (*1*) weight loss; (*2*) DTA; and (*3*) differential curve of weight loss.

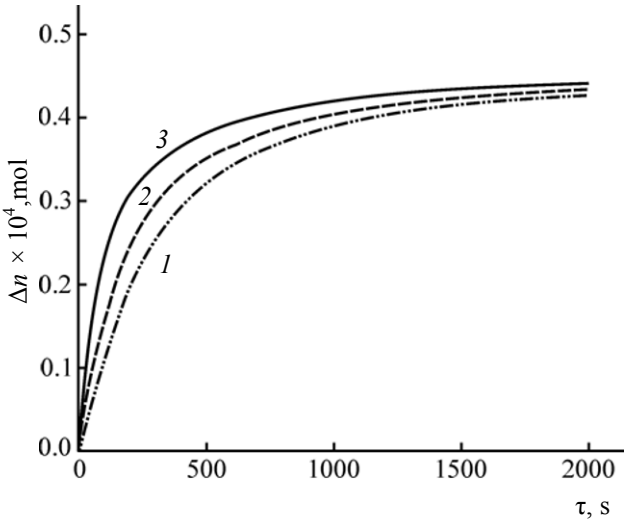

Fig. 3. Absorption of oxygen in the system ferrocene–benzoyl peroxide (acetonitrile, 25°C ($[BP]_0 = 10^{-2}$ M): (*1*) $[CP_2Fe]_0 = 2 \times 10^{-2}$ M; (*2*) $[CP_2Fe]_0 = 4 \times 10^{-2}$ M; and (*3*) $[CP_2Fe]_0 = 6 \times 10^{-2}$ M.

The consumption of ferrocenium radical-cation in the reaction with molecular oxygen can be ascribed to the formation of [μ-(peroxy-*O*:*O*')]diferrocenium benzoate.

The product of the reaction of ferrocenium with BP we obtained in isooctane at room temperature in oxygen atmosphere. The grey-blue precipitate is stable in the solid state at storage during 3 months. ^{1}H NMR spectrum in ethanol-d_6 contains a singlet at δ 5.35 ppm belonging to the cyclopentadienyl ring, and two multiplets at δ 6.55, 7.05 ppm belonging to the benzoate anion. In the IR spectrum of the product, characteristic absorption bands of the benzoate anion (1653, 1400 cm^{-1}), of aromatic ring (1250, 1100–950 cm^{-1}), O–O bonds (880 cm^{-1}) and Fe–C (476 cm^{-1}) are observed. Iodometric analysis of the product showed the presence of peroxide (95.5%).

Consumption of molecular oxygen in the reaction of ferrocene with benzoyl peroxide in various solvents, T = 25°C, V = 4 mL

Solvent	$n_0(Cp_2Fe)$, μmol	n_0(BzOOBz), μmol	$\Delta n(O_2)$, μmol	$w_0 \times 10^2$, μmol/s
Acetonitrile	80	40	43.7	12.4
	160	40	44.0	13.5
	240	40	44.6	30.1
Ethanol	80	40	31.6	15.5
Isooctane	80	40	24.6[a]	0.40
p-Xylene	80	40	28.0[a]	0.95
	20	10	11.3	0.10
	40	10	10.7	0.24
	80	10	9.5	0.30

[a] ($[Cp_2Fe^+]PhCO_2^-$) is precipitated.

The results of thermogravimetric analysis of the reaction product of ferrocene with benzoyl peroxide in isooctane in oxygen atmosphere are shown in Fig. 2. The curve of the mass loss has a section at 50–320°C typical for decomposition of peroxides, and a further decrease in the weight of the sample with small exothermic effect.

In the presence of oxygen the consumption of the ferrocenium radical-cation is observed, which is formed in the reaction of ferrocene with benzoyl peroxide. Using the method of differential manometry [14] it was found that solutions of $[Cp_2Fe^+]PhCO_2^-$ consume molecular oxygen. For precise determination of the amount of the consumed oxygen the ferrocene radical-cation was generated in the cell of the manometric installation. Consumption of molecular oxygen was observed during the reaction (Fig. 3). The results are presented in the table.

As follows from the table, ferrocenium radical-cation reacts with 0.5 mol of molecular oxygen at the ferrocene to benzoyl peroxide ratio of 2 : 1 in all the studied solvents. Further increase of the ferrocene amount with respect to benzoyl peroxide does not affect the amount of the consumed oxygen, which

corresponds to the stoichiometry of the reaction. The initial rate of the oxygen consumption increases with polarity of the solvent, apparently, due to a decrease in the redox potential of ferrocene in polar solvents [15] and increase in the rate of generation of the radical-cation.

Therefore, it has been shown that in oxygen atmosphere oxygen takes part in the reaction of ferrocene with benzoyl peroxide. The stoichiometry of the reaction ferrocene : oxygen is determined to be 2 : 1, which corresponds to the stoichiometry of the reaction of ferrocenium radical-cation with molecular oxygen with the formation of [μ-(peroxy-*O*:*O*')]diferrocenium benzoate.

EXPERIMENTAL

Ferrocene (Fluka) was used without preliminary purification. Benzoyl peroxide was crystallized thrice from ethanol and dried at room temperature in a vacuum to a constant mass.

Electron absorption spectra were registered on a Specord M40 UV-Vis spectrophotometer in the range 200–800 nm in quartz cells of l = 0.1–1.0 cm with the corresponding solvent as the reference solution.

IR spectra were recorded on a Specord M80 spectrophotometer in the range 4000–250 cm^{-1} from suspensions in mineral oil. NMR spectra were registered on a Bruker AV-500 spectrometer.

Reaction of molecular oxygen with ferrocenium benzoate. The solution of ferrocene (100 mg, 0.54 mmol) in 10 mL of isooctane was added at 30°C to the solution of benzoyl peroxide (65 mg, 0.27 mmol) in 40 mL of isooctane saturated with oxygen. After 1.5 h the formed precipitate was filtered and washed with isooctane (3 × 5 mL) and dried in a vacuum. Yield 59 mg (54%). Found, %: C 60.50, H 4.59. $C_{34}H_{30}Fe_2O_6$. Calculated, %: C 63.15, H 4.64.

The sample (~0.01–0.05 g) was dissolved in glacial acetic acid, 1 mL of saturated solution of KI was added, the mixture was stirred in the dark for 20 min. The formed iodine was titrated with 0.01–0.05 N solution of $Na_2S_2O_3$. In parallel a blank experiment was performed. The mass fraction of the peroxide in percent was calculated by the formula: $x = N_{TS}V_{TS}M \times 100/1000m2$, where N_{TS} is the normality of the solution of $Na_2S_2O_3$, V_{TS} is the volume of $Na_2S_2O_3$ solution used for titration corrected for the blank experiment, mL; m is the mass of the specimen, g; M is molecular mass of peroxide.

IR and NMR spectra were recorded in the center of joint usage "Chemistry" in Institute of Organic Chemistry of Russian Academy of Sciences.

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