

Spectral studies of the mechanism of oxidation of Cp_2Fe by ozone

R. G. Bulgakov,* L. I. Sharapova, G. L. Sharipov, and G. G. Bikbaeva

*Institute of Petrochemistry and Catalysis, Academy of Sciences of Republic of Bashkortostan,
Ufa Research Center of the Russian Academy of Sciences,
141 prosp. Oktyabrya, 450071 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750*

The mechanism of oxidation of Cp_2Fe by ozone in CCl_4 was studied by chemiluminescence (CL), photoluminescence, IR, UV, and NMR spectral techniques. Ozone attacks Cp_2Fe at the $\text{Fe}-\text{C}$ and $\text{C}=\text{C}$ bonds to form peroxides CpOOFe , CpFeOOH , triplet ($3\pi^*$) ketones (CL emitters), and organic acids.

Key words: ferrocene, ozone, chemiluminescence, photoluminescence.

Ferrocene Cp_2Fe is stable toward oxygen^{1–3} but can easily be oxidized by ozone.^{4–6} However, literature data on the products and mechanism of the reaction of ferrocene with ozone are lacking. We have previously reported⁷ the chemiluminescence (CL) during oxidation of Cp_2Fe by ozone. In this work, the mechanism of this reaction in CCl_4 was studied by spectral methods.

Experimental

Ferrocene was synthesized according to the procedure described previously.⁸ In the study of CL, an O_3 +air mixture was used for ozonization (an Ozonid SP ozonator, 0.4 mmol h^{-1}), and for the determination of reaction products, an O_3 + O_2 mixture was used (an Ozon-4K ozonator, 8 mmol h^{-1}). Carbon tetrachloride was purified by the known procedure,⁹ and its purity was monitored by GLC and UV spectroscopy. Solutions of Cp_2Fe ($(2\text{--}5) \cdot 10^{-2}\text{ mol L}^{-1}$) were prepared by dissolution of a weighed sample in CCl_4 . Ozone was introduced into a solution of Cp_2Fe through a glass bubbler. Oxidation products were analyzed after the separation and washing of the precipitate that formed (precipitate 1) from the solution by centrifuging. After this procedure, the solution contained 25–30% of the starting amount of Cp_2Fe . The solution and precipitate 1 were analyzed for the content of iron (by trilonometry¹⁰) and Cl^- ions (according to Volhard). The reaction products were separated from a heated (45°C) oxidized solution of Cp_2Fe by condensation with an N_2 flow into a trap filled with liquid N_2 . The condensate was heated to 40°C , and the air-dry precipitate (precipitate 2) was dissolved in isooctane to study UV spectra.

Chemiluminescence was recorded on an installation described previously.¹¹ A FEU-39 photomultiplier was used as the light receiver. CL spectra were measured using a set of boundary light filters. Photoluminescence (PL) spectra were recorded on a spectrofluorimeter mounted on the base of an MDR-23 double-resolution monochromator. UV and IR spectra were obtained on Specord M-40 and Specord IR-75 spectrophotometers, respectively. ^{13}C NMR spectra of the oxidized solutions of Cp_2Fe were obtained on a JEOL FX-90Q NMR spectrometer (22.5 MHz, $\text{CCl}_4+\text{C}_6\text{D}_6$ as the solvent).

Results and Discussion

The oxidation of Cp_2Fe by ozone in CCl_4 is accompanied by CL for 5–6 min in the beginning of the reaction, change in color from orange to dark-brown, and formation of a precipitate, which results in a loss of transparency of the solution and a decrease in the CL intensity. In the initial period of passing O_3 , the CL intensity is $I_{\text{max}} = (0.7\text{--}1.2) \cdot 10^7\text{ photon s}^{-1}\text{ mL}^{-1}$ (Fig. 1). The CL spectrum contains a broad band with $\lambda_{\text{max}} = 460\text{ nm}$ (Fig. 2). The starting reagents and final oxidation products (the oxidate obtained 20 min after passing of O_3) have no PL in CCl_4 (300 and 77 K).

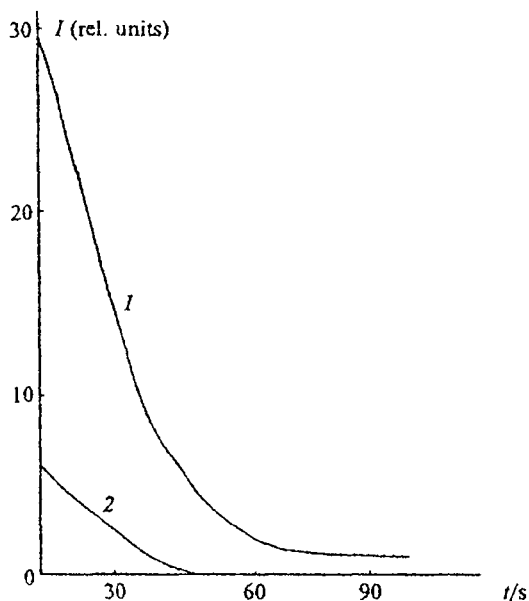


Fig. 1. Time dependences of the CL intensity: 1, in the reaction of Cp_2Fe ($10^{-2}\text{ mmol L}^{-1}$) with ozone; 2, in contact of CCl_4 with ozone. The total volume of CCl_4 is 5 mL.

Thus, intermediate products of oxidation, presumably ketones, which have been identified in the products of oxidation by oxygen of cyclopentadienides of many metals,^{2,3,12-14} are emitters of CL. In this work, we obtained spectral data that confirm the formation of ketones in the ground energy state during oxidation of Cp_2Fe by ozone. We ruled out singlet-excited ketones as emitters, because the fluorescence spectra of partially oxidized solutions (5–10 min) differ from the CL spectrum ($\lambda_{\text{max}} = 460$ nm, see Fig. 2) by the position of a maximum ($\lambda_{\text{max}} = 580$ nm). At the same time, the CL spectrum correlates well with the phosphorescence spectra obtained¹² for 4-cyclopentene-3,5-dione and dicyclopentadienone. The formation of these ketones in the reaction of Cp_2Fe with O_3 is confirmed by the characteristic IR absorption bands (1709 , 1773 cm^{-1} for dicyclopentadienone and 1747 cm^{-1} for 4-cyclopentene-3,5-dione).

It can be assumed that the simplest ketone that is present in this system (cyclopentadienone) can also act as a CL emitter. However, this ketone is rapidly dimerized¹² ($k = 10^8$ s^{-1}), which impedes its identification.

After 25–30 min of ozonization, the initial UV spectrum of Cp_2Fe , (CCl_4 , $\lambda_{\text{max}}/\text{nm}$: 325 (ϵ 51), 440 (ϵ 81)) exhibits a weak decrease in the intensity of the band at 440 nm (due to the cleavage of the $\text{Fe}-\text{C}$ bond) and an almost doubling of the intensity of the band at $\lambda_{\text{max}} = 325$ nm due to the substitution of the Cp ligand

by an electron-withdrawing substituent.⁸ The UV spectrum of precipitate 1 dissolved in a 0.1 M aqueous solution of HCl contains bands at 377 and 625 nm, which indicates the formation of $[\text{Cp}_2\text{Fe}]^+$.

The IR absorption spectra of precipitate 1 exhibit intense bands with maxima at 1610 cm^{-1} ($\text{C}=\text{C}$), 1705 cm^{-1} ($\text{C}=\text{O}$), 1285 cm^{-1} , and 3400 cm^{-1} (OH^-), as well as a broad band at 1580 cm^{-1} (COO^-), indicating the decomposition of the Cp ring. The ^{13}C NMR spectrum (CCl_4) contains a signal at 166 ppm characteristic of the COO^- group. During the reaction, the intensity of the IR absorption band at 478 cm^{-1} ($\text{Fe}-\text{C}$) decreases and intensities of the bands at 1580 cm^{-1} (COO^-), 1700 cm^{-1} ($\text{C}=\text{O}$), 3400 cm^{-1} (OH^-), and 1050 cm^{-1} increase (Fig. 3). It can be assumed that the absorption band at 1050 cm^{-1} is due to the formation of ozonides from the Cp ring. This band was observed for ozonization of several organic substances and attributed¹⁵ to stretching vibrations of the $\text{C}-\text{O}$ bond of ozonides.

Elemental analysis of precipitate 1 corresponds to the empirical formula $\text{C}_8\text{H}_9\text{O}_8\text{FeCl}_{0.4}$. The products of oxidation of metallocenes by dioxygen usually have the empirical composition^{1,2} $\text{C}_{10}\text{H}_{10}\text{O}_4 \cdot \text{MO}_2$ ($\text{M} = \text{V}, \text{Cr}, \text{and Ni}$). We believe that a lower content of carbon in our case is related to decomposition of the Cp ring by ozone. The products also contain chlorine, which indicates that the solvent participates in the ozonolysis of Cp_2Fe .

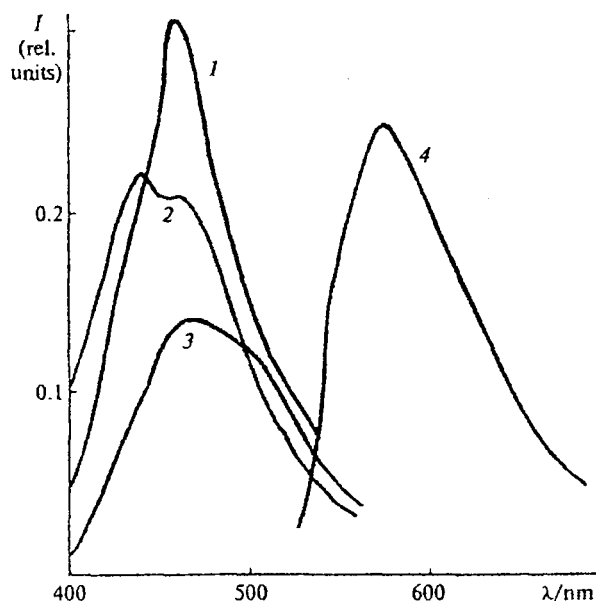


Fig. 2. Results of spectral studies of ferrocene oxidation: 1, CL spectrum for oxidation of Cp_2Fe (10^{-2} mol L^{-1}) by ozone in CCl_4 ; 2 and 3, phosphorescence spectra ($\lambda_{\text{exc}} = 300$ nm) of 4-cyclopentene-3,5-dione and dicyclopentadienone,¹² respectively; and 4, PL spectrum ($\lambda_{\text{exc}} = 365$ nm) of a solution of Cp_2Fe in CCl_4 (10^{-2} mol L^{-1}) partially oxidized by ozone.

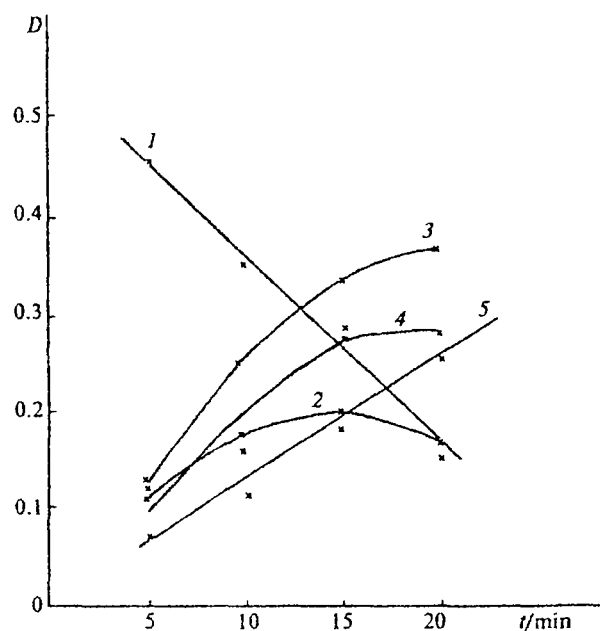
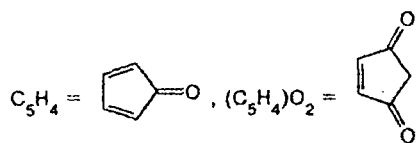
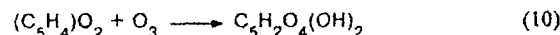
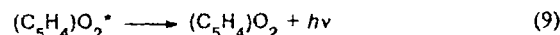
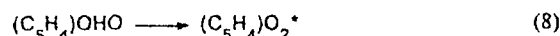
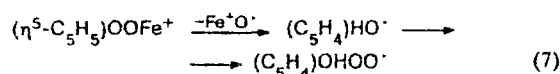
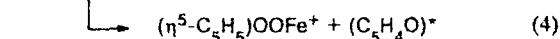
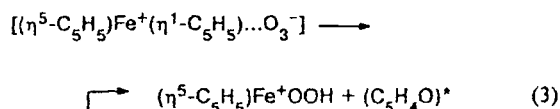
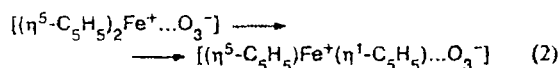
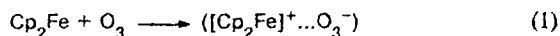


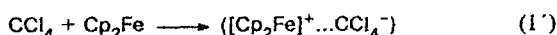
Fig. 3. Dependences of the optical absorption density (D) of several bands in the IR absorption spectrum of precipitate 1 on the time of ozonization of Cp_2Fe ($[\text{Cp}_2\text{Fe}]_0 = 0.1$ mol L^{-1}) in CCl_4 : 1, 478 cm^{-1} ($\text{Fe}-\text{C}$); 2, 1050 cm^{-1} ; 3, 1580 cm^{-1} (COO^-); 4, 1700 cm^{-1} ($\text{C}=\text{O}$); and 5, 3400 cm^{-1} (OH^-).

The data obtained made it possible to propose a general scheme of the ozonization of Cp_2Fe in CCl_4 (Scheme 1).

Scheme 1



According to the published data,¹⁶ ferrocene exists in a CCl_4 solution as a charge transfer complex (CTC).



We detected this CTC by the corresponding absorption band at 307 nm in the UV spectrum. The absorption band ($\lambda = 620$ nm) characteristic of the $[\text{Cp}_2\text{Fe}]^+$ cation does not appear before contact with O_3 . The formation of $[\text{Cp}_2\text{Fe}]^+$, whose presence is confirmed by the characteristic UV spectrum ($\lambda_{\text{max}} = 620$ nm (CCl_4)) of the filtrate and organic part of precipitate 1, is the primary step of oxidation. After electron transfer, one of the $\eta^5\text{-C}_5\text{H}_5\text{Fe}$ bonds is transformed into $\eta^1\text{-C}_5\text{H}_5\text{Fe}$ (reaction (2)), which is indicated by the appearance in the IR spectrum of the absorption band at 1500–1600 cm^{-1} attributed to stretching vibrations of the $>\text{C}=\text{C}<$

bond. Then dioxygen can also participate in the oxidation of $[\text{Cp}_2\text{Fe}]^+$.² To evaluate the possibility of the contribution of this reaction to CL, the $[\text{Cp}_2\text{Fe}]^+$ cation was synthesized using an independent method by the UV irradiation ($\lambda_{\text{max}} = 260$ nm) of a solution of Cp_2Fe (10^{-3} mol L^{-1}) in an argon atmosphere. Chemiluminescence was not observed when dioxygen was passed through this solution, i.e., the contribution of oxidation of $[\text{Cp}_2\text{Fe}]^+$ and the products of its interaction with dioxygen to CL is insufficient. Thus, unlike the known¹⁷ CL during autooxidation of metallocenes (Ln, Cr, and U), the appearance of CL of ferrocene requires the action of a stronger oxidant such as ozone. At the same time, according to the published data,² the oxidation of $[\text{Cp}_2\text{Fe}]^+$ by dioxygen gives the same products (ketones based on the Cp ring) as the oxidation of cyclopentadienyls of the metals mentioned. Therefore, one of the important reasons for the absence of CL during the oxidation of $[\text{Cp}_2\text{Fe}]^+$ by oxygen can be the considerably lower rate of this process² than that of the interaction of Cp_2Fe with O_3 .

The intermediate complex, the product of electron transfer from Cp_2Fe to O_3 , is further transformed in reactions (3) and (4) into compounds containing O—O peroxy groups. This is indicated by the appearance of the IR absorption band at 830–890 cm^{-1} . (In this system, the positive indication of a reaction with KI at the O—O group is incorrect because of the impeding interaction of KI with ozone that can hardly be removed from CCl_4 .) Iron peroxide (reaction (3)) and $(\eta^5\text{-C}_5\text{H}_5)\text{OOFe}^+$ (reaction (4)), which are products of ozonization, can appear in the reaction mixture.

Simultaneous appearance of two types of peroxides is also characteristic^{1,4} of the oxidation of other organo-metallic compounds. The catalytic oxidation by dioxygen of cyclopentadiene (CPD) occurred because the elimination of H atoms from the solvent by the Cp radical is one of the most important pathways of the formation of ketones during oxidation of metallocenes.^{2,14} In the system under question, this route is improbable because the solvent (CCl_4) contains no hydrogen. We assume that excited ketones are formed simultaneously with hydroperoxide (reaction (3)) and organoiron peroxide (reaction (4)) as well as in the decomposition of the latter (reaction (7)). Ketone appearing at stages (3) and (4) is sufficiently rapidly dimerized by reaction (6), which is indicated by the IR spectrum containing absorption bands at 1709 and 1773 cm^{-1} characteristic of the ketone dimer.

The fact that the COO^- group was identified among the ozonization products indicates that O_3 also attacks the Cp ring, affording organic acids by reaction (10). Cyclopentadiene reacts with ozone both before and after dimerization (which is not shown in Scheme 1).

It was established by the addition of a radical inhibitor (ionol) that free radical reactions do not proceed either in dark or light processes of the oxidation of Cp_2Fe by ozone.

Thus, during the ozonization of Cp_2Fe , ozone attacks both the $\text{Cp}-\text{Fe}$ bond to form peroxides and ketones and the double bonds of the Cp ring to form organic acids.

The authors are grateful to V. N. Odínokov and V. R. Akhmetova for help in ozonization and to L. M. Khalilov and A. Z. Sharipova for measuring NMR spectra.

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Received September 15, 1998