Kinetics and mechanism of photolysis of the iron(III) complex with tartaric acid

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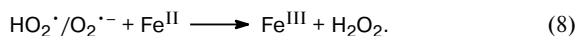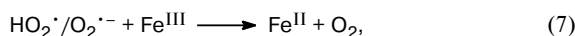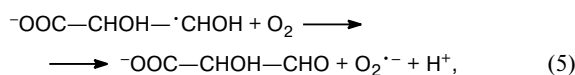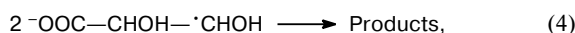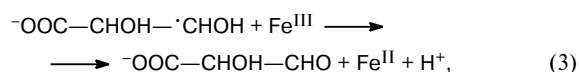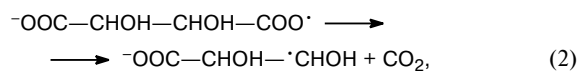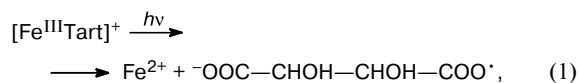*Fax: +7 (383) 330 7350. E-mail: glebov@ns.kinetics.nsc.ru*
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The formation of $MV^{\bullet+}$ radical cations was observed upon the laser flash photolysis of the iron(III) tartrate complex $[Fe^{III}Tart]^+$ (**1**) in the presence of methyl viologen (MV^{2+}). The rate constants of the reactions involving $MV^{\bullet+}$ were measured. The intramolecular electron transfer to form Fe^{II} and escape of the organic radical to the solvent bulk upon the photolysis of **1** were proposed.

Key words: photochemistry, Fe^{III} complexes, carboxylic acids, aqueous solutions, UV spectra, laser flash photolysis.

Photochemistry of iron(III) complexes with organic ligands substantially affects the balance of organic compounds in natural aqueous systems.[1,2] In the two recent decades, photolysis of the Fe^{III} complexes with anions of carboxylic acids has been intensively studied.[1-12] The photolysis mechanism was proposed on the basis of analysis of the final products of photochemical reactions.[1-9] Direct experiments on observation of intermediate photolysis products are very rare.

The mechanism of photolysis proposed on the basis of analysis of the final reaction products includes the intramolecular electron transfer to form iron(II) and the escape of the organic radical to the solvent bulk as the primary act. The primary free radical can be decarboxylated, and the resulting secondary radical reacts with different components of the system (for instance, with Fe^{III} and dioxygen). The typical scheme of reactions of the Fe^{III} complex with tartaric acid is presented by Eqs (1)—(8) (similar scheme is known for the photolysis of the Fe^{III} citrate complex[6]). Reactions (5)—(8) are excluded when experiments are carried out in the absence of O_2.

$$[Fe^{III}Tart]^+ \xrightarrow{h\nu}$$
$$\longrightarrow Fe^{2+} + {}^-OOC-CHOH-CHOH-COO^{\bullet}, \quad (1)$$

$${}^-OOC-CHOH-CHOH-COO^{\bullet} \longrightarrow$$
$$\longrightarrow {}^-OOC-CHOH-{}^{\bullet}CHOH + CO_2, \quad (2)$$

$${}^-OOC-CHOH-{}^{\bullet}CHOH + Fe^{III} \longrightarrow$$
$$\longrightarrow {}^-OOC-CHOH-CHO + Fe^{II} + H^+, \quad (3)$$

$$2\,{}^-OOC-CHOH-{}^{\bullet}CHOH \longrightarrow Products, \quad (4)$$

$${}^-OOC-CHOH-{}^{\bullet}CHOH + O_2 \longrightarrow$$
$$\longrightarrow {}^-OOC-CHOH-CHO + O_2^{\bullet-} + H^+, \quad (5)$$

$$O_2^{\bullet-} + H^+ \rightleftharpoons HO_2^{\bullet}, \quad (6)$$

$$HO_2^{\bullet}/O_2^{\bullet-} + Fe^{III} \longrightarrow Fe^{II} + O_2, \quad (7)$$

$$HO_2^{\bullet}/O_2^{\bullet-} + Fe^{II} \longrightarrow Fe^{III} + H_2O_2. \quad (8)$$

The mechanisms of the photoreactions proposed on the basis of analysis of the final products require to be experimentally confirmed by the detection of assumed intermediates. However, the use of direct experimental methods (laser flash photolysis) for the determination of the primary processes in the photochemistry of carboxylate complexes of transition metals is difficult, because the assumed intermediate species have no intense absorption bands in the visible or near-UV spectral region. The exception is Fe^{III} oxalate, whose laser excitation affords an intermediate with the intense absorption at 400 nm: presumably, a Fe^{II} complex with an organic radical.[9]

Detection of weakly absorbing intermediates requires the use of acceptors: compounds that react with the radical under study to produce an intermediate with the intense characteristic absorption. This approach is exemplified by the proof of hydroxyl radical formation upon the photolysis of the Fe^{III} hydroxo complexes (see Refs 10 and 13—16).

The purpose of the present work is a search for efficient acceptors of short-lived intermediate species formed
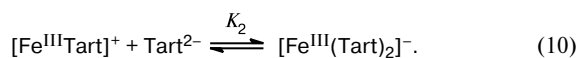
upon the photolysis of the [Fe^{III}Tart]$^+$ complex. This approach can be extended to Fe^{III} complexes with other carboxylic acids.

Experimental

Spectra of intermediate compounds and the kinetics of absorbance changes were studied by a laser flash photolysis technique using excitation by a XeCl laser (308 nm, pulse duration 20 ns, pulse energy 20 mJ).[17] Iron(III) perchlorate and tartaric acid with concentrations of the both reactants $5 \cdot 10^{-4}$ mol L^{-1} at pH 3.0 were used to synthesize the [Fe^{III}Tart]$^+$ complex. The solutions were purged with argon for 15 min to remove oxygen.

Results and Discussion

The following processes occur in solution during the reaction of Fe^{III} with tartaric acid:

$$Fe^{3+} + Tart^{2-} \underset{K_1}{\rightleftharpoons} [Fe^{III}Tart]^+, \qquad (9)$$

$$[Fe^{III}Tart]^+ + Tart^{2-} \underset{K_2}{\rightleftharpoons} [Fe^{III}(Tart)_2]^-. \qquad (10)$$

Under the above described conditions, reactions (9) and (10) are characterized by the stability constants $\log K_1 = 7.49$ and $\log K_{1,2} = 11.86$ (see Ref. 18), and 86% Fe^{III} ions are bound in the [Fe^{III}Tart]$^+$ complex.

The UV spectrum of the complex is shown in Fig. 1 (curve *1*).

The methyl viologen dication (MV^{2+}) was used as the acceptor of intermediate radicals.
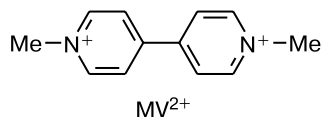
Me$-$N$^+$ ⬡ ⬡ N$^+$$-$Me

MV^{2+}

Methyl viologen dichloride hydrate (Aldrich) was used as the source of the MV^{2+} ions. This compound was chosen because of the reduction properties of the $^-$COOH$-$CHOH$-^{\cdot}$CHOH radical formed due to the decarboxylation of the $^-$COOH$-$CHOH$-$CHOH$-$COO$^{\cdot}$ primary radical (reactions (1) and (2)). Previously MV^{2+} was multiply used as a scavenger of reducing radicals in experiments on pulse radiolysis[19—23] and flash photolysis.[24—26] The optical spectrum of the MV^{2+} dication (see Fig. 1, curve *2*) has a weak absorption at the wavelength of laser radiation ($\varepsilon_{308} = 425$ L mol^{-1} cm^{-1}). The used concentrations of MV^{2+} and the iron(III) complex are close and, therefore, the main absorbing species is the [Fe^{III}Tart]$^+$ complex for which $\varepsilon_{308} = 6250$ L mol^{-1} cm^{-1}.

The photolysis of a solution of [Fe^{III}Tart]$^+$ in the absence of MV^{2+} results in a decrease in the absorbance in the region of the absorption band of the starting complex (Fig. 2, *a*). Thus, the intermediate species are characterized by the very weak absorption at 300—800 nm. The
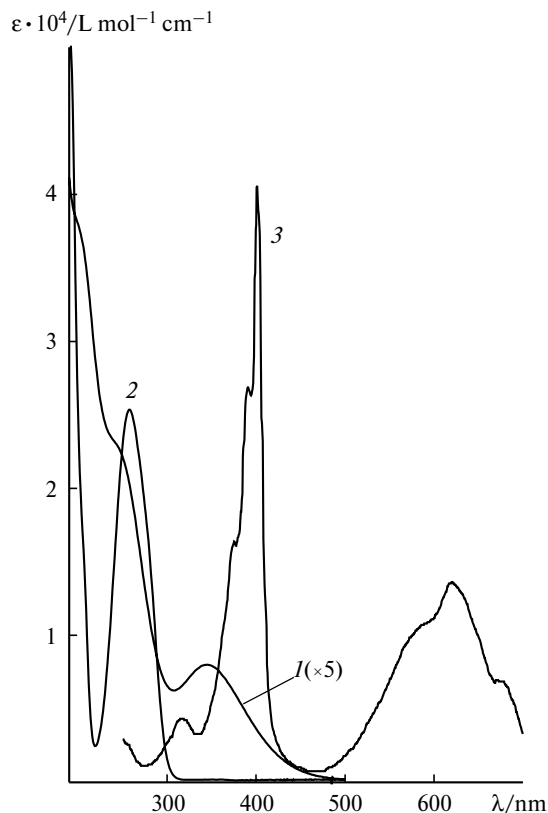
Fig. 1. UV absorption spectra of aqueous solutions of the [Fe^{III}Tart]$^+$ complex at pH 3.0 (*1*), methyl viologen dication MV^{2+} at pH 5.5 (*2*), and radical cation MV$^{\cdot +}$ (*3*).

absence of changes in the concentration of the [Fe^{III}Tart]$^+$ complex in the time interval shorter than 400 µs indicates a low rate constant of reaction (3) ($k_3 < 5 \cdot 10^5$ L mol^{-1} s^{-1}).

The kinetic curves for absorption changes of [Fe^{III}Tart]$^+$ after the addition of MV^{2+} are shown in Fig. 2, *b*. The differential absorption spectrum appeared upon the photolysis of [Fe^{III}Tart]$^+$ in the presence of MV^{2+} is presented in Fig. 3, *a*. The absorption bands at 370—400 nm and a less intense absorption band with a maximum at 605 nm are observed against the background of the absorbance decrease caused by the decay of the starting complex. These bands belong to the MV$^{\cdot +}$ radical cation[27—29] (Fig. 1, curve *3*).

The MV$^{\cdot +}$ radical cation is formed due to two processes. First, this is the direct photolysis of the methyl viologen dication, whose molar absorption coefficient at the laser radiation wavelength (308 nm) is 430 L mol^{-1} cm^{-1} (Fig. 1, curve *2*). This photoreaction is known.[30] It is most likely that the direct formation of the radical cations occurs due to the photolysis of the [MV^{2+}(Cl$^-$)] complexes. When fitting the kinetic curves, the formation of MV$^{\cdot +}$ directly in photolysis was taken into account by the introduction of a low (~10^{-7} mol L^{-1}) initial concentration of the methyl viologen radical cation.
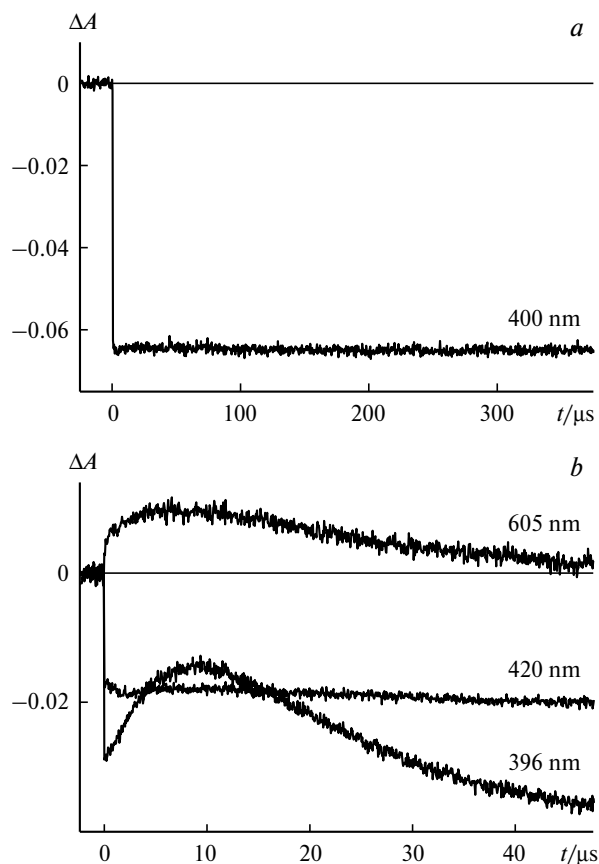
Fig. 2. Kinetic curves detected during laser flash photolysis (308 nm) of aqueous solutions (pH 3.0) of the $[Fe^{III}Tart]^+$ complex ($5 \cdot 10^{-4}$ mol L^{-1}) (temperature 298 K, cell thickness 1 cm, argon purging for 15 min) at the methyl viologen concentration 0 (*a*) and $1 \cdot 10^{-3}$ mol L^{-1} (*b*).

In addition, the MV$^{\cdot+}$ radical cation is formed by the reaction of MV^{2+} with the organic radical anion. We assumed that this is the radical anion $^-COOH—CHOH—^{\cdot}CHOH$ formed due to the decarboxylation of the primary $^-COOH—CHOH—CHOH—COO^{\cdot}$ radical anion (reaction (2)). If the solution contains no oxygen and other oxidants, the concentration of the MV$^{\cdot+}$ radical cations remains unchanged within several minutes.[27,28] In our case, the decay rate of the radical cations increased with an increase in the concentration of the initial complex, indicating that the reaction occurs between MV$^{\cdot+}$ and $[Fe^{III}Tart]^+$.

The proposed kinetic scheme of reactions involving methyl viologen includes the following reactions (in addition to reactions (1)—(8)):
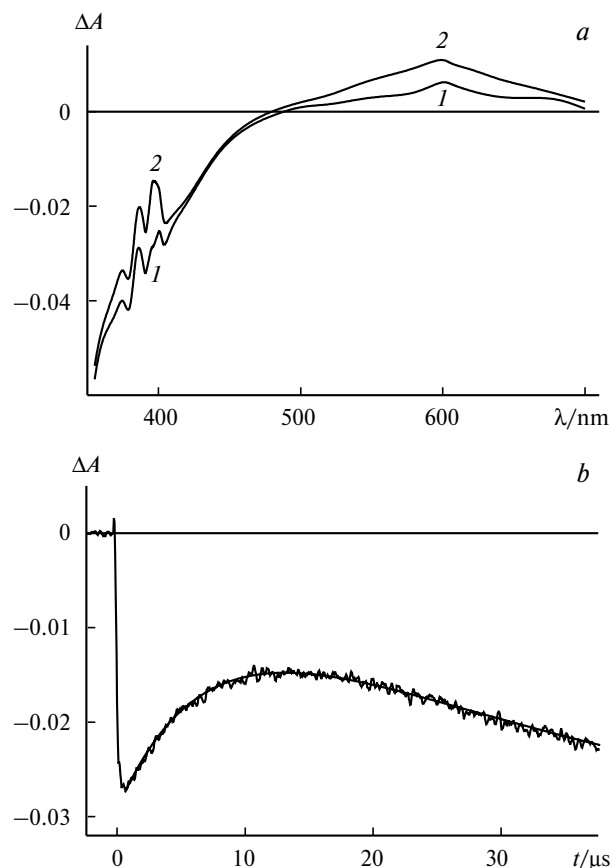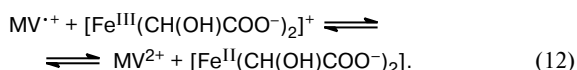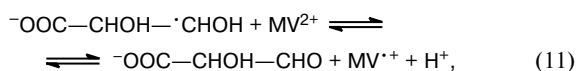
$$^-OOC—CHOH—^{\cdot}CHOH + MV^{2+} \rightleftharpoons$$
$$\rightleftharpoons \, ^-OOC—CHOH—CHO + MV^{\cdot+} + H^+, \quad (11)$$

$$MV^{\cdot+} + [Fe^{III}(CH(OH)COO^-)_2]^+ \rightleftharpoons$$
$$\rightleftharpoons \, MV^{2+} + [Fe^{II}(CH(OH)COO^-)_2]. \quad (12)$$

Fig. 3. Laser flash photolysis (308 nm) of deaerated aqueous solutions (pH 3.0) of the $[Fe^{III}Tart]^+$ complex ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of MV^{2+} ($1 \cdot 10^{-3}$ mol L^{-1}); *a*, differential absorption spectra recorded 0 (*1*) and 8 (*2*) μs after laser pulse; *b*, example for the calculation of the kinetic curve of formation and decay of the MV$^{\cdot+}$ radical cations (396 nm) at the methyl viologen concentration $4 \cdot 10^{-4}$ mol L^{-1}. Smooth line is the approximation of the kinetic curve due to the solution of the system of differential equations corresponding to reactions (4), (11), and (12) with the rate constants $2k_4 = 1.2 \cdot 10^9$ L mol^{-1} s^{-1}, $k_{11} = 4.0 \cdot 10^6$ L mol^{-1} s^{-1}, and $k_{12} = 2.3 \cdot 10^8$ L mol^{-1} s^{-1}.

The standard reduction potential of the MV^{2+}/MV$^{\cdot+}$ redox pair relative to the hydrogen electrode is -0.45 V (see Ref. 31). Based on analysis of published data on the redox potentials for aldehydes and ketones, we could expect a value lying in the range from -1 to -2 V for the $^-OOC—CHOH—CHO$, H$^+$/$^-OOC—CHOH—^{\cdot}CHOH$ redox pair (see Ref. 31). As a result, the equilibrium of reaction (11) should be shifted to the right, which is confirmed by an increase in the intensity of the absorption bands of the MV$^{\cdot+}$ radical cation (see the initial regions of the kinetic curves in Fig. 2, *b*). The redox potential of the $[Fe^{III}(CH(OH)COO^-)_2]^+/[Fe^{II}(CH(OH)COO^-)_2]$ pair is positive, and the equilibrium in reaction (12) should also be shifted to the right.

Calculation of the kinetic curve of MV$^{\cdot+}$ radical cation decay by the solution of the system of differential

equations corresponding to reactions (4), (11), and (12) is exemplified in Fig. 3, *b*. These reactions represent a minimum set that makes it possible to describe the kinetic curves. The calculations were performed under the assumption that the rate constant of decarboxylation (2) is $\geq 10^7\ s^{-1}$. In this case, the initial concentration of the $^{-}OOC—CHOH—^{\bullet}CHOH$ radical anions can be considered equal to the decrease in the concentration of the starting $[Fe^{III}Tart]^{+}$ complex under laser pulse irradiation. Published data on the rate constants of decarboxylation of radicals of the $^{-}OOC—CHOH—CHOH—COO^{\bullet}$ type having no absorption in the spectral region available for detection are lacking. The decarboxylation rate constants of various aryloxy radicals with an intense absorption in the visible spectral region lie in the interval from 10^6 to $5 \cdot 10^7\ s^{-1}$ (see Ref. 32).

Below we present the average rate constants obtained by the calculation of the set of kinetic curves corresponding to the concentration of $[Fe^{III}Tart]^{+}$ $4.3 \cdot 10^{-4}\ mol\ L^{-1}$ and MV^{2+} concentrations $(1—4) \cdot 10^{-4}\ mol\ L^{-1}$ (pH 3.0, the ionic strength of the solution was varied within the interval $(3.6—5.4) \cdot 10^{-3}\ mol\ L^{-1}$; the molar absorption coefficient of the $MV^{\bullet +}$ radical cation at the wavelength 396 nm was accepted in the calculations to be $41\ 500\ L\ mol^{-1}\ cm^{-1}$ (see Ref. 27)):

Reaction	(4)	(11)	(12)
$k/L\ mol^{-1}\ s^{-1}$	$(6\pm2) \cdot 10^8$	$(4.4\pm0.6) \cdot 10^6$	$(1.8\pm0.6) \cdot 10^8$

Thus, the detection of the $MV^{\bullet +}$ radical cation in experiments on laser flash photolysis of $[Fe^{III}Tart]^{+}$ unambiguously indicates that the system contains a radical with the reduction properties (in our case, $^{-}OOC—CHOH—^{\bullet}CHOH$) and confirms the mechanism of photolysis of $[Fe^{III}Tart]^{+}$ (see reactions (1)—(8)) proposed on the basis of analysis of the final products of the photoreactions.

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