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Reply to "Comment on 'New insight into Photochemistry of Ferrioxalate'"

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There are two different points of view on the primary photoprocess following the excitation of the $Fe^{III}(C_2O_4)_3{}^{3-}$ complex:

M1. Intramolecular electron transfer from the ligand to the Fe(III) ion. The long-lived excited state, the radical complex $[(C_2O_4)_2Fe^{II}(C_2O_4{}^{\bullet})]^{3-}$, or the $C_2O_4{}^{\bullet-}$ radical is assumed to be the primary intermediate(s).[1–3]

M2. The sequential cleavage of Fe(III)−O bond (between one oxalate ligand and Fe(III) ion) and the C−C bond of the ligand. Biradical complex[4] $[(C_2O_4)_2Fe^{III}(CO_2{}^{\bullet})_2]^{3-}$ or tetrahedral-like $Fe(III)(C_2O_4)_2{}^-$ complex and $CO_2{}^{\bullet-}$ radical[5,6] are assumed to be primary intermediates.

In our recently published work[3] we used nanosecond flash photolysis to study the photochemistry of the $Fe^{III}(C_2O_4)_3{}^{3-}$ complex. We found that excitation of $Fe^{III}(C_2O_4)_3{}^{3-}$ at 355 nm led to the formation of two long-lived species absorbing in the near UV region. Lifetimes of both species depend on initial concentrations of ligand and ferrioxalate but do not dependent on the concentration of oxygen. These findings are in agreement with results of previous works.[1,2,5,6] What is more important, the yield of radicals ($CO_2{}^{\bullet-}$ and $C_2O_4{}^{\bullet-}$) was less than 6% relative to the $Fe^{III}(C_2O_4)_3{}^{3-}$ depletion. This observation allows us to reject mechanism M2 and to propose that mechanism M1 takes place.

Our results and interpretation do not agree with work by Rentzepis' group where mechanism M2 was proposed to explain photochemistry of $Fe^{III}(C_2O_4)_3{}^{3-}$ complex.[6] Below we discuss the results of both groups and try to find the possible reasons for such a discrepancy.

1. Primary Yield of Radical Species ($CO_2{}^{\bullet-}$ and $C_2O_4{}^{\bullet-}$). For the detection of organic radicals in flash photolysis experiments we used methyl viologen dication (MV^{2+}), which is a well-known electron acceptor.[7,8] MV^{2+} reacts with both $CO_2{}^{\bullet-}$ and $C_2O_4{}^{\bullet-}$ radicals with high rate constants ($k = 1 \times 10^{10}$ M^{-1} s^{-1} and $k = 4.3 \times 10^9$ M^{-1} s^{-1}, respectively).[7] The cation-radical $MV^{\bullet+}$ produced in these reactions exhibits strong absorptions at 396 nm ($\varepsilon = 41\,500$ M^{-1} cm^{-1}) and 605 nm.[9]

Our results (namely the negligible primary yield of radical species) contradict the results of indirect radical-scavenging experiments performed by Rentzepis' group.[6] They observed a large, more than 50% drop of quantum yield of Fe(II) upon addition of thymine into ferrioxalate solution. This drop in quantum yield was attributed to the thymine scavenging the $CO_2{}^{\bullet-}$ radical formed in the primary photoprocess.

In the Comments our colleagues from the Rentzepis' group suggested that this discrepancy is due to our underestimation of $MV^{\bullet+}$ yield in flash experiments. They proposed several possible reasons for such underestimation that are discussed below.

1. Reactions between the $MV^{\bullet+}$ Radical with Possible Oxidizers ($C_2O_4{}^{\bullet-}$, $CO_2{}^{\bullet-}$, and Ferrioxalate), Which May Greatly Decrease the Observed Yield of $MV^{\bullet+}$. Indeed, $MV^{\bullet+}$ can react with possible oxidizers, such as $C_2O_4{}^{\bullet-}$ ($k = 7 \times 10^{10}$ M^{-1} s^{-1}, ref 7) and $Fe^{III}(C_2O_4)_3{}^{3-}$. However in our experimental conditions ($[Fe^{III}(C_2O_4)_3{}^{3-}] = 1.6 \times 10^{-4}$ M, $MV^{2+} = 1 \times 10^{-3}$ M, $[R^{\bullet}] < 2 \times 10^{-5}$ M) the formation of $MV^{\bullet+}$ takes less than 100 ns while its lifetime is more than 3 μs (ref 3, Figure 3, curve 5, p 8319). So by 100 ns after the laser pulse (the moment used for $MV^{\bullet+}$ yield calculation) only a negligible part of $MV^{\bullet+}$ radicals disappears in the reactions with possible oxidizers. It also can be calculated that under the experimental conditions used in ref 3 more than 94% of organic radicals are quenched by methyl viologen.

2. Great Decrease of the Rate Constant (k_1) of Reaction between MV^{2+} and Organic Radical Resulting from the Increased Ionic Strength. According to ref 7 only 25% decrease of k_1 is observed when the ionic strength is increased from 0 to 0.1. In ref 3 we directly measured k_1 and found it to be equal 1.2×10^{10} M^{-1} s^{-1} in our experimental conditions.

3. Direct Photolysis of Methyl Viologen. It is well-known[10] that UV excitation of concentrated aqueous solution of MV^{2+} leads to the direct photoreduction of $MV^{2+}(Cl)_2$ to $MV^{\bullet+}(Cl)$. This is why we used low concentration of MV^{2+} ($\leq 1 \times 10^{-3}$ M) and excited the ferrioxalate in the presence of MV^{2+} at 355 nm, where absorption of MV^{2+} is negligible ($\varepsilon(MV^{2+}$, 355 nm) < 5 M^{-1} cm^{-1}).[7] We also performed flash photolysis experiments on aqueous solutions of MV^{2+} ($[MV^{2+}] = 10^{-3}$ M) without ferrioxalate and did not observe the formation of $MV^{\bullet+}$.

So we conclude that the primary yield of organic radicals is rather small.

As we commented in ref 3 the drop of quantum yield of Fe(II) in the presence of scavenger that our colleagues from the Rentzepis' group observed can be attributed to other factors rather than quenching of $CO_2{}^{\bullet-}$ by thymine. The drop could be explained by oxidation by thymine of final Fe(II)−oxalate complexes or the transient species, or by complexation of Fe(II) ions with thymine. It is also not obvious why such a poor $CO_2{}^{\bullet-}$ radical scavenger as thymine was chosen by Rentzepis' group. According to the Comment the reaction rate constant between thymine and the $CO_2{}^{\bullet-}$ radical is only 5×10^4 M^{-1} s^{-1}. The use of more efficient scavenger and utilization of a time-resolved technique such as laser flash photolysis would allow us to compare the results of our groups more directly.

2. Nature of Long-Lived Intermediate Fe(II) and Fe(III) Oxalate Complexes. In both works[3,6] the successive formation of two intermediates (further referred to as In1 and In2) absorbing in the near UV ($\lambda_{max} \approx 400$ nm) was observed in nanosecond flash photolysis experiments. The difference in lifetimes of In1 (110 ns[6] versus 20 μs[3]) and In2 (0.63 ms[6] versus 1 ms[3]) observed in ref 6 and our work[3] is most probably due to the difference in experimental parameters such as pH and the concentration of oxalate ions and $Fe^{III}(C_2O_4)_3{}^{3-}$.[2,3,5]

In our work[3] In1 is believed to be to the primary radical complex, $[(C_2O_4)_2Fe^{II}(C_2O_4{}^{\bullet})]^{3-}$ (RC1), formed via intramolecular electron transfer and In2 to be secondary radical complex, $[(C_2O_4)Fe^{II}(C_2O_4{}^{\bullet})]^-$ (RC2), formed via reversible dissociation of RC1. Our hypothesis was based on the following:

1. The $Fe^{III}(C_2O_4)_3{}^{3-}$ complex was excited at the wavelength of charge-transfer (CT) band.

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2. We observed only negligible yield of organic radicals in primary photoprocess.

3. The formation of long-lived radical complexes is a common case in the photochemistry of transient metals, which was shown for the number of coordination compounds (including oxalate complexes of Fe(III) and Co(III)).[1,2,11−13] The stability of RC1 could be explained by the large structural changes in the radical Fe(II)−oxalato complex. It is known that the Fe−O bond in Fe(II)−oxalate complexes is significantly longer (by ∼0.2 Å) (ref 6 and references herein) than the corresponding bond in Fe(III)−oxalate. This structural difference may result in a potential barrier preventing back electron transfer.

4. Successive formation of RC1 and RC2 explains the observed dependence of lifetimes of transient species on initial concentrations of $Fe^{III}(C_2O_4)_3{}^{3-}$ and free ligand (see ref 3 for details).

Our colleagues in ref 6 presented an alternative explanation of the nature of intermediate species. In1 was assigned to the tetrahedral-like four-coordinated $Fe^{III}(C_2O_4)_2{}^{-}$ complex formed in reaction 1:

$$*[Fe^{III}(C_2O_4)_3{}^{3-}] \rightarrow Fe^{III}(C_2O_4)_2{}^{-} + 2CO_2{}^{\bullet -} \qquad (1)$$

In2 was assigned to the $Fe^{II}(C_2O_4)_3{}^{4-}$ complex formed in the diffusion-controlled reaction of $CO_2{}^{\bullet -}$ with the initial complex (reaction 2):

$$Fe^{III}(C_2O_4)_3{}^{3-} + CO_2{}^{\bullet -} \rightarrow Fe^{II}(C_2O_4)_3{}^{4-} + CO_2 \qquad (2)$$

The latter species undergo reversible dissociation (reaction 3), which explains the observed dependence of In2 lifetime upon ligand concentration:

$$Fe^{II}(C_2O_4)_3{}^{4-} \Leftarrow\ \Rightarrow Fe^{II}(C_2O_4)_2{}^{2-} + C_2O_4{}^{2-} \qquad (3)$$

Both assignments were based upon agreement of the experimental values of Fe−O bond length measured by EXAFS with results of theoretical calculations for these oxalate complexes.

There are several serious reservations about nature of aforesaid transient species:

1. $CO_2{}^{\bullet -}$ radical is a very strong reductant (($E^0(CO_2/CO_2{}^{\bullet -})$ = −2.0 V[8]) and reacts with diffusion-controlled rate constants with Fe(III)−oxalate complexes.[3,6]

2. Both coordinatively unsaturated, tetrahedral $Fe^{III}(C_2O_4)_2{}^{-}$ and $Fe^{II}(C_2O_4)_2{}^{2-}$ could undergo rather fast thermal aquation yielding stable oxalate complexes that do not absorb at 400 nm.[3]

3. The $Fe^{II}(C_2O_4)_3{}^{4-}$ complex cannot be stabilized at any concentration of the ligand used in ref 6 (see ref 3 for the formation constants of Fe(II)−oxalate complexes) so the reaction 3 cannot explain the observed dependence of the In2 lifetime upon ligand concentration. Moreover, it is unlikely that the $Fe^{II}(C_2O_4)_3{}^{4-}$ complex has an absorption maximum at 400 nm (as postulated in ref 6) because both $[Fe^{II}(C_2O_4)_2(H_2O)_2]^{2-}$ and $[Fe^{II}(C_2O_4)(H_2O)_4]$ complexes have absorption maxima ≤350 nm and exhibit only negligible absorption at 400 nm[3].

4. Reaction 1 should be a minor photoprocess as the primary yield of the $CO_2{}^{\bullet -}$ radical is found to be negligible.[3]

3. Nature of Primary Photoprocess. The colleagues in the Comment indicated that our paper[3] did not present any time-resolved data in the picosecond time range in which both intramolecular electron transfer and dissociation processes are known to occur and we did not comment on the results of time-resolved EXAFS experiments published in ref 6 which strongly contradict our data and conclusions.

We completely agree that both intramolecular electron transfer and dissociation processes should be fast or even ultrafast (less than several picoseconds). And (unfortunately) our time resolution is not sufficient in comparison with EXAFS and ultrafast optical spectroscopy data presented in ref 6, so we can freely discuss only the nature of intermediates existing in time window 50 ns to 1 ms. Also, ref 6 did not present the experimental evidence that the $Fe^{III}(C_2O_4)_3{}^{3-}$ complex is a main species in EXAFS experiments. At the concentration of ferrioxalate used in ref 6 (1.6 M) the formation of dimeric or even polynuclear species could be possible (in fact, this behavior is a typical for Fe(III) complexes[14−16]). So the fruitful discussion and interpretation of EXAFS data[6] seems to be problematic. Nevertheless, below we try to do it by assuming that $Fe^{III}(C_2O_4)_3{}^{3-}$ is a main species in all experimental conditions.

The great elongation of the Fe−O bond by 0.15 Å (EXAFS) and formation of the transient absorption spectrum with a maximum at 430 nm (pump−probe experiments) were observed after excitation of $Fe^{III}(C_2O_4)_3{}^{3-}$, which was assigned to the formation of the excited state of the complex in which Fe ions retain its +3 oxidation level.[6] On the contrary we suggest that the primary short-lived intermediate observed in both EXAFS and pump−probe experiments is the excited state of $Fe^{III}(C_2O_4)_3{}^{3-}$ in which partial electron transfer takes place. This suggestion coincides with the assignment of the UV band in Fe(III)−oxalate complexes to the charge-transfer band[17] and with the fact that the Fe−O bond length in the excited state (2.16 Å) observed by EXAFS corresponds to the bond lengths in Fe(II) oxalate complexes (2.1−2.2 Å).[6]

The excited state of $Fe^{III}(C_2O_4)_3{}^{3-}$ decays very fast, and at 4 and 9 ps after excitation the Fe−O bond length is 1.93 and 1.87 Å, respectively. The authors[6] assign the intermediates observed by EXAFS at times 4 and 9 ps to the 5-coordinate $[(C_2O_3)O{-}Fe^{III}(C_2O_4)_2]^{3-}$ and 4-coordinate $Fe^{III}(C_2O_4)_2{}^{-}$ complexes. This assignment is based on agreement of experimental Fe−O bond lengths with results of theoretical calculations (DFT).

For reasons we discussed above, the $Fe^{III}(C_2O_4)_2{}^{-}$ is hardly to be an important transient species in $Fe^{III}(C_2O_4)_3{}^{3-}$ photochemistry. We can give the alternative explanations of EXAFS data published in ref 6, which is in an agreement with our results obtained by nanosecond flash photolysis.

The usual situation in photochemistry of coordination compounds is that the primary excited state populated upon a LMCT type transition undergoes fast conversion to the long-lived thermally equilibrated secondary excited state (THEXI state).[17] So one can tentatively assume that variation of Fe−O bond length during the first 10 ps after excitation is linked to population and thermal relaxation of the THEXI state. One evidence of THEXI state formation is independence (or weak dependence) of quantum yield of photolysis on the excitation wavelength. As the quantum yield of $Fe^{III}(C_2O_4)_3{}^{3-}$ photolysis depends weakly on the excitation wavelength,[18] the assumption of the intermediate THEXI state is quite reasonable. Decay of the THEXI state leads to formation of the radical complex RC1 observed by nanosecond flash photolysis.

Finally, we fully agree with the remark of our colleagues that the absorption spectra of transient tetrahedral-like $Fe^{III}(C_2O_4)_2{}^{-}$ and $Fe^{II}(C_2O_4)_2{}^{2-}$ complexes can differ from the absorption spectra of the stable hydrated complexes $[Fe^{III}(C_2O_4)_2(H_2O)_2]^{-}$ and $[Fe^{II}(C_2O_4)_2(H_2O)_2]^{2-}$.

In summary, one can conclude that the mechanism of $Fe^{III}(C_2O_4)_3^{3-}$ photolysis (especially the primary stage of this mechanism) is still open for discussion. A deeper insight into the photochemistry of ferrioxalate demands the combination of quantum chemistry calculations with detailed investigation of spectral and kinetic behavior of transient species in a wide range of time scales from hundreds of femtoseconds to hundreds of milliseconds.

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