Dynamics of adduct formation of hydroquinone under oxidative conditions observed by laser spectroscopy

Victor Nadtochenko† and John Kiwi

Institute of Physical Chemistry II, Swiss Federal Institute of Technology, Lausanne 1015, Switzerland

Hydroxylated products of hydroquinone (H_2Q) are induced *via* $[Fe(ox)_3]^{3-}$–H_2O_2 under light and detected in the visible region by laser spectroscopy; reaction of hydroxyl radicals with (H_2Q) is observed leading to adduct formation.

During the past few years the photochemistry of tris(oxaloferrate) has been studied.[1,2] Work has been reported recently[3,4] of the reactions of this complex with organic compounds using steady-state photolysis, flash photolysis and stopped-flow in the millisecond region and at longer times. Here, we report on the reactions of $[Fe(ox)_3]^{3-}$–H_2O_2 with hydroquinone (H_2Q) from the nanosecond timescale upwards. The findings reported here aim to further our understanding[4–7] about the mode of intervention of $[Fe(ox)_3]^{3-}$ during the degradation of H_2Q in oxidative media.

$FeCl_3$, dihydrooxalic acid and hydroquinone were all Fluka p.a. and used as received. Laser photolysis was carried out using the second harmonic (λ = 347 nm) of a JK-2000 ruby laser operated in the Q-switched mode. The pulse width was *ca.* 10 ns and the energy *ca.* 10 mJ per pulse. The detection of the transient absorption changes was performed *via* an EGG photomultiplier with a rise time of *ca.* 5 ns. The basic system for kinetic spectroscopy detection has been described previously.[8]

Fig. 1(*a*) presents the transient species after the laser pulse for the traces (*i*) H_2Q (40 mm) reacting with H_2O_2 (0.29 mm), (*ii*) $[Fe(ox)_3]^{3-}$ reacting with H_2O_2 (0.29 mm), (*iii*) the transient decay of $[Fe(ox)_3]^{3-}$ (0.6 mm) back to the ground state or to a metastable longer lived[6] intermediate $[(ox)_2Fe(ox^{\cdot-})]$ **I** (Scheme 1).

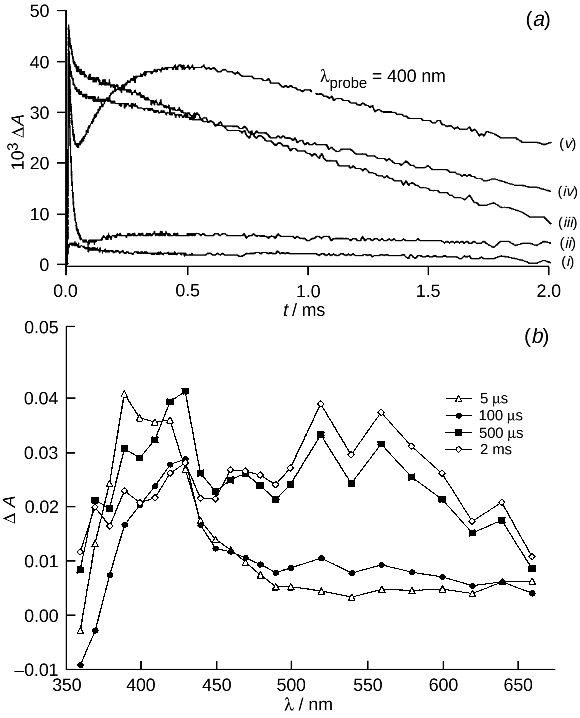


Fig. 1 (*a*) Laser transients for different solutions of $[Fe(ox)_3]^{3-}$, H_2O_2 and hydroquinone (H_2Q). For other experimental details see text. (*b*) Transient decay spectra as a function of λ for the system $Fe(ox)_3{}^{3*-}$ [oxalate (0.6 mm)–Fe^{3+} (18 mm), H_2Q (40 mm) and H_2O_2 (0.29 m) at pH 6.5].

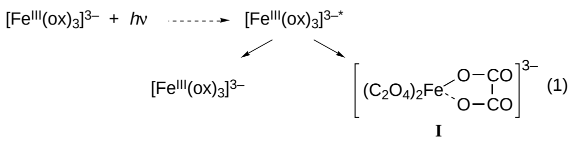
Trace (*iv*) in Fig. 1(*a*) shows $[Fe(ox)_3]^{3-}$ decay in the presence of H_2Q (40 mm) where a quenching effect is noticeable. Finally, to this solution is added H_2O_2 (0.29 m) and the result is shown in Fig. 1(*a*) trace (*v*). The lifetimes (τ) of $[Fe^{III}(ox)_3]^{3-*}$ and **I** are *ca.* 5 μs and 2 ms, respectively, at neutral pH. The disappearance of the initial transient absorption is followed by the formation of a coloured species within *ca.* 600 μs. This is observed only in trace (*v*) for the complete chemical system $[Fe(ox)_3]^{3-}$–H_2O_2–H_2Q. It is not possible to rationalize this result in terms of formation of $^{\cdot}OH$ radicals by the usual Fenton mechanism [eqn. (2)][1,4] since (*a*) the

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH; \quad k_2 = 41\text{–}75\ \mathrm{m^{-1}\ s^{-1}} \qquad (2)$$

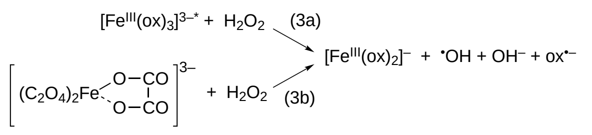
characteristic time for the reaction is about 10^3 times longer[9] than the values observed in Fig. 1(*a*) when $[Fe(ox)_3]^{3-}$–H_2O_2 is photolysed in solution and (*b*) the observed rise time of the coloured product in Fig. 1(*a*) is seen to be close to the lifetime of the transient $[Fe(ox)_3]^{3-*} + H_2O_2$ as shown in Fig. 1(*a*) trace (*ii*). It is therefore impossible to assign the observed $^{\cdot}OH$ radical formation to the mechanism of eqn. (2) since only fast intermediates having lifetimes of microseconds would be able to hydroxylate H_2Q. Radical formation could be accounted for by reaction of $[Fe^{III}(ox)_3]^{3-*}$ or **I** with H_2O_2[6] (Scheme 2).

It has been previously reported[10] that $k_{OH + H_2Q} = 1.2 \times 10^{10}$ $\mathrm{m^{-1}\ s^{-1}}$. Since H_2Q (40 mm) was used in Fig. 1(*a*), trace (*i*), the characteristic time for $^{\cdot}OH$ radical attack would be *ca.* 2.1×10^{-9} s. The second pathway of Scheme 2 [eqn. (3*b*)] therefore should be the limiting step for $^{\cdot}OH$ radical formation when $[Fe^{III}(ox)_3]^{3-*}$ reacts with H_2O_2 under light leading subsequently to adduct formation with H_2Q as observed in trace (*v*) of Fig. 1(*a*). This conclusion is confirmed by the near independence observed for the formation of the coloured product of H_2Q on the H_2Q concentration in the range 2–40 mm at fixed H_2O_2 and $[Fe^{III}(ox)_3]^{3-}$ concentrations [as shown in Fig. 2(*b*)].

Fig. 1(*b*) shows the absorbances of the products formed after the laser pulse. Different transient lifetimes and absorbances (*A*) were observed as a function of λ due to the existence of different coloured intermediate transients between 350 and 550 nm. The



Scheme 1



Scheme 2

signals in Fig. 1(*b*) at λ = 450 nm and beyond would correspond to oxidized H_2Q–OH adducts in agreement with work by Adams and Michael[10] using pulse radiolysis. The spectrum at 5 μs after the pulse is mainly due to the initial quenching of the binary system $[Fe(ox)_3{}^{3-}]$–H_2Q by H_2O_2. Kinetics of H_2Q hydroxylation consistent with the observations can be rationalized by Schemes 1–3. The rate constants used have been previously reported.[11–13]

Under the experimental conditions used, $[H_2O_2] \gg [Fe^{2+}]$, $[H_2O_2] \gg [ox^{2-}]$ and $[H_2O_2] \gg [\cdot OH]$. The solution for this

$$H_2Q + {}^{\bullet}OH \longrightarrow H_2Q\text{–}OH(adduct) \qquad k_4 = 1.2 \times 10^{10}\,M^{-1}s^{-1} \quad (4)$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow HO_2{}^{\bullet} + H_2O \qquad k_5 = 1.3 \times 10^{7}\,M^{-1}s^{-1} \quad (5)$$

$$ox^{2-} + {}^{\bullet}OH \longrightarrow OH^- + ox^{\bullet-} \qquad k_6 = 2 \times 10^{6}\,M^{-1}s^{-1} \quad (6)$$

$${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \qquad k_7 = 5.3 \times 10^{9}\,M^{-1}s^{-1} \quad (7)$$

$${}^{\bullet}OH + Fe^{2+} \longrightarrow OH^- + Fe^{3+} \qquad k_8 = 3 \times 10^{8}\,M^{-1}s^{-1} \quad (8)$$

Scheme 3

$$[Fe(ox)_3{}^{3-*}] / dt = -k_q[Fe(ox)_3{}^{3-*}] - k_a[H_2O_2][Fe(ox)_3{}^{3-*}] \qquad (9)$$

$$d[{}^{\bullet}OH] / dt = k_a[H_2O_2][Fe(ox)_3{}^{3-*}] - k_5[{}^{\bullet}OH][H_2O_2] - k_4[{}^{\bullet}OH][H_2Q] \qquad (10)$$

$$d[adduct] / dt = k_4[{}^{\bullet}OH][H_2Q] \qquad (11)$$

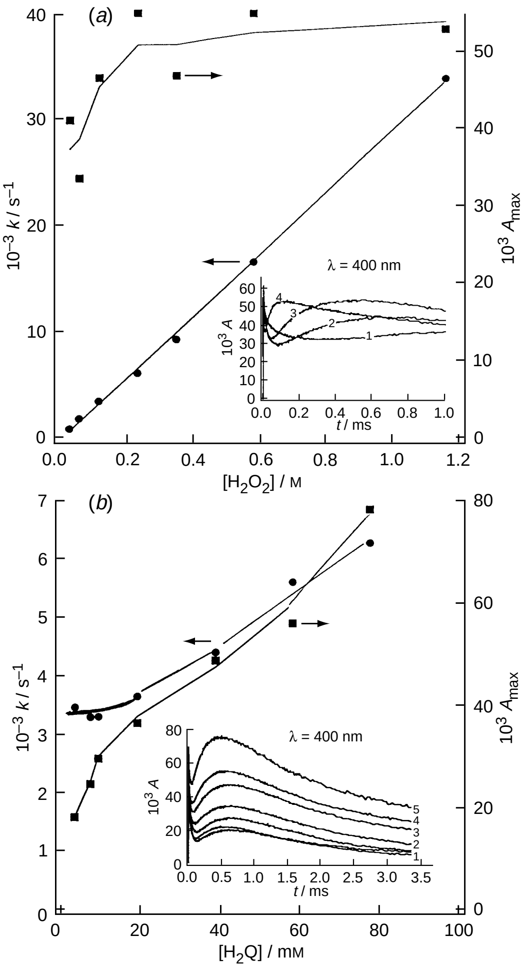


Fig. 2 (*a*) Dependency of the reciprocal rise time of hydroquinone adducts (●) and absorbance A_{max} (■) *vs.* H_2O_2 concentration. The same solution as in Fig. 1(*b*) was used. The insert shows the transient at λ = 400 nm when H_2O_2 is added at concentrations of (*i*) 0.029, (*ii*) 0.12, (*iii*) 0.58 and (*iv*) 1.16 m. (*b*) Dependency of the reciprocal rise time of hydroquinone (H_2Q) adducts (●) and absorbance A_{max} (■) as a function of H_2Q concentration. The insert shows the transient at λ = 400 nm when H_2Q has been added in the following concentrations: (*i*) 10, (*ii*) 20, (*iii*) 39, (*iv*) 59 and (*v*) 79 mm.

system of differential equations can be stated in a simplified form

$$\Delta A(t) = A_{max} - (cte)\ \exp\{-(k_q + k_a[H_2O_2])t\} \qquad (12)$$

where $A_{max} = k_4k_a[H_2O_2][H_2Q][Fe(ox)_3{}^{3*-}]_0/(k_q + k_a[H_2O_2])(k_5[H_2O_2] + k_4[H_2Q])$ and $(cte) = k_4k_a[H_2O_2][H_2Q][Fe(ox)_3{}^{3-*}]_0/\{[(k_5[H_2O_2] + k_4[H_2Ql]) - k_q + k_a[H_2O_2])](k_q + k_a[H_2O_2])\}$.

Fig. 2(*a*) and (*b*) show the dependency of the reciprocal rise time k/s^{-1} and maximum amplitude for the coloured products (A_{max}) as a function of H_2O_2 and H_2Q concentrations. Fig. 2(*a*) shows the dependency for k/s^{-1} *vs.* $[H_2O_2]$ for a solution oxalate 18 mm–Fe^{3+} 0.6 mm at pH 6.5 and $[H_2Q]$ = 59 mm. The insert in Fig. 2(*a*) shows the traces due to the coloured adduct formation (*A*) for different concentrations of added H_2O_2 in the millisecond range. The linear dependency of k/s^{-1} *vs.* H_2O_2 in Fig. 2(*a*) with slope $2.9 \pm 0.4 \times 10^5$ m^{-1} s^{-1} is observed to be close to the value of the quenching reported[5] for $[Fe(ox)_3]^{3-*}$. This suggests the formation of ·OH radicals in reaction (3) as the limiting step for H_2Q hydroxylation. This result is consistent with the relation $k/s^{-1} = k_q + k_a[H_2O_2]$. In the latter equation at high H_2O_2 concentrations $k_a[H_2O_2] > k_q$, the value of A_{max} would be independent of the oxidant concentration. In effect Fig. 2(*a*) shows that the value of A_{max} is almost independent of H_2O_2 concentration above *ca.* 0.25 m.

Fig. 2(*b*) shows the rate constant when experiments similar to those in Fig. 2(*a*) were carried out. The H_2O_2 concentration was kept constant at 0.145 m while the concentration of H_2Q was varied in the range 2–78 mm. The growth of the transient at λ = 400 nm is shown in the insert. The value of A_{max} near saturation at H_2Q concentrations of 20–40 mm further increases at $[H_2Q] > 40$ mm. A kinetic model over the entire concentration range studied in Fig. 2 is not capable of accounting for all the features associated at higher H_2Q concentrations.

This work has presented insight into adduct formation of H_2Q–OH. Fast hydroxylation of H_2Q can only be explained by the presence of the ·OH radicals due to the fast reaction rate of ·OH with H_2Q.[10]

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Footnote

† On leave of absence, Institute of Chemical Physics, Russian Academy of Sciences. Chernogolovka 142432, Moscow Region, Russia.

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