Detection of Intermediate Species in Electron Transfer between Iron(III) Nitrate and Hydroquinone by Millisecond Time-resolved *X*-Ray Absorption Spectroscopy in Dispersive Mode

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Time-resolved *X*-ray absorption spectroscopy in the dispersive mode has been applied as a fast (5 ms) *X*-ray absorption monitor to obtain spectra (7.08—7.23 keV) and rate constants of electron transfer between iron(III) nitrate and hydroquinone in methanolic aqueous solution.

There are a variety of methods available to monitor the progress of a chemical reaction in solution.[1] At present, monitoring methods such as UV-VIS spectrophotometry, fluorescence, circular dichroism, resonance Raman, light scattering, NMR, and EPR spectroscopies, and conductivity are widely applied to rapid reaction monitoring techniques with flow methods. The availability of a number of monitoring techniques is important for a complete description of the reaction scheme, since different parts of the overall mechanism may respond to different physical probes.[1]

In studies of solution redox reactions, UV-VIS spectral monitoring remains the most important general method for determining the rates of rapid processes, and is facilitated by the change of the electronic absorption band of the bound ligand and/or the charge transfer band of the complex formed in the redox reaction. On the other hand, EXAFS spectroscopy is a powerful method to monitor the change in local structure at the periphery of the metal atom of the complex in solution.[2]

Attempts to apply EXAFS methods to fast time-resolved spectroscopy, especially with the aim of determining the local fine structure of reactive intermediates of a rapid reaction in solution, command considerable attention.[3] Using energy dispersive *X*-ray absorption spectroscopy,[4—6] a wide energy-range profile of an absorption spectrum can be recorded simultaneously without any mechanical motion during the measurements, which is suitable for time-resolved *X*-ray absorption spectroscopy. Preliminary results of time-resolved experiments using dispersive *X*-ray absorption spectrometers have been reported by Matsushita,[7] Fontaine,[8] Sayers,[9] and Maire.[10]

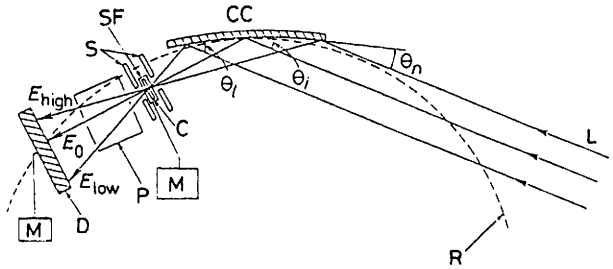
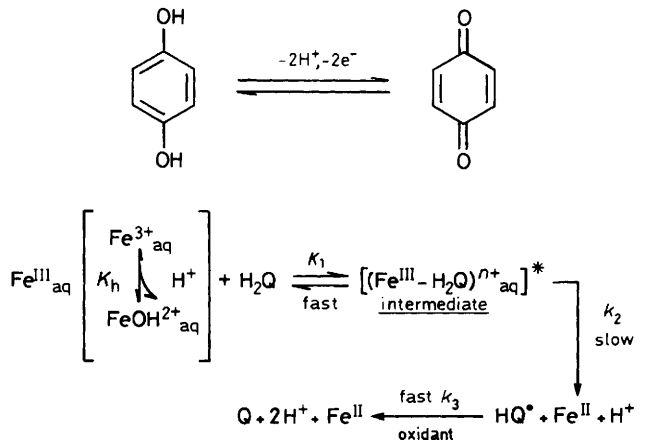


Figure 1. Scheme of the time-resolved *X*-ray absorption spectrometer in the dispersive mode: M, microcomputer; D, photodiode array (Reticon RL1024-SF and Gd_2O_2S : Tb screen); P, Pt-coated mirror; S, slit; SF, remote-controlled stopped-flow apparatus; C, stopped-flow cell (4 × 6 × 1 mm path length) with two 100 μm thick tensioned Mylar windows); CC, triangularly-cut single-crystal monochromator [Si(111)]; R, Rowland circle; L, synchrotron radiation source at 2.5 GeV and 100—260 mA.

In this communication, we report the construction of an *X*-ray absorption stopped-flow spectrometer[11] (Figure 1) suitable for recording the *X*-ray absorption spectra of transient species of the redox reaction between hydroquinone and iron(III) nitrate in acidic methanolic aqueous solution. This apparatus allows far more specific identification of such species than is possible with a conventional UV-VIS stopped-flow spectrometer.

The redox reactions of hydroquinone (H_2Q) with various oxidizing agents are complicated because these involve both protons and electrons.† Using iron(III) perchlorate as an oxidizing agent the redox reaction scheme in dilute aqueous solutions (10^{-3}—10^{-2} mol dm^{-3}) *via* the formation of intermediate semiquinones has been reported in detail.[12] However, the presence of such an intermediate species was not proved directly by the spectroscopic method.

In concentrated solutions (0.1—0.6 mol dm^{-3}), the formation of blue intermediate species was clearly demonstrated by rapid-scan spectroscopy‡ and was also observed as a change in the colour of the solution from initially pale purple, *via* blue,



Scheme 1

† In dilute solutions (10^{-2}—10^{-3} mol dm^{-3}), the stoicheiometry of the reaction is found to be $2Fe^{3+} + H_2Q \rightarrow 2Fe^{2+} + Q + 2H^+$, judging from the disappearance of the absorption at $\lambda_{max.}$ (292 nm) of H_2Q on addition of Fe^{3+} aqua ion.

‡ Using a rapid-scan spectrometer, the transient broad absorption spectrum ranging from 510 to 650 nm is obtained immediately (<5 ms) after mixing the solutions of H_2Q (0.2 mol dm^{-3}) and Fe^{3+} aqua ion (0.2 mol dm^{-3}). This broad absorption band rapidly decays within 1—2 s.

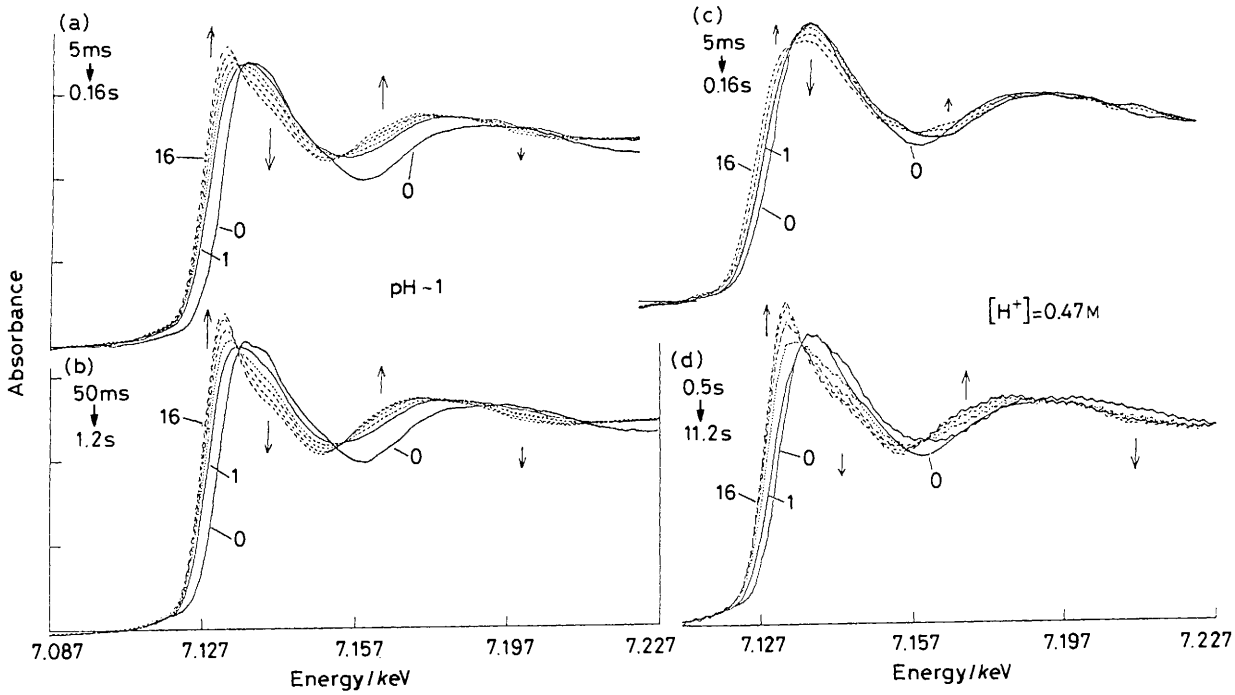


Figure 2. Transient XANES spectra (Fe-*K* edge) accompanying the electron-transfer process between Fe^{3+} aqua ion (0.3 mol dm^{-3}) and hydroquinone (0.3 mol dm^{-3}) in a methanol–water [50% (v/v)] mixed solvent system: (a) 5, 15, 35, 75, 160 ms (exposure time 5 ms, interval time 5 ms, 400 scans); (b) 50, 125, 275, 585, 1200 ms (exposure time 50 ms, interval time 25 ms, 150 scans) at pH ~1; (c) 5, 15, 75, 160 ms (exposure time 5 ms, interval time 5 ms, 400 scans); (d) 0.5, 1.2, 2.6, 5.4, 11.2 s (exposure time 500 ms, interval time 200 ms, 15 scans) at $[H^+]$ = 0.47 mol dm^{-3}. The total data collection time per spectrum is *ca.* 21—30 min using an *X*-ray absorption stopped-flow spectrometer.

to brown. In general, the overall redox reaction (inner-sphere mechanism) is divided into three steps, formation of the intermediate species (fast process; step 1), electron transfer and decomposition of the intermediate complex (slow process; step 2), and the formation of the final oxidized product (step 3).[13,14] However, in the hydroquinone system, the distinction between steps 2 and 3 is obscure.§ Since the observed rates decreased with increasing acidity, both Fe^{3+} and its corresponding hydroxy species $FeOH^{2+}$ were considered to be involved and the mechanism shown in Scheme 1 has been proposed, consistent with the kinetic data.¶ It involves a prior one-electron extraction from H_2Q (through an intermediate species, [ ]*) yielding a species $HQ^{\cdot}$–Fe^{II} which is decomposed and further oxidized to *p*-quinone, Q($k_2 \ll k_3$).

It is important to note that while the energy-dispersive mode is ideal for the time-resolved studies, this mode is not applicable to samples in low concentrations (10^{-3}—10^{-5} mol dm^{-3}). Highly concentrated samples (> 0.1 mol dm^{-3}) are needed for absorption EXAFS measurements in the transmission mode. Figure 2 shows the time-resolved XANES spectra (Fe-*K* edge) accompanying the inner-sphere electron transfer reaction between the Fe^{3+} aqua ion and hydroquinone at high concentrations (0.3 mol dm^{-3}), which are collected using the Synchrotron Radiation Source on Beam Line 4A of the Photon Factory (KEK at Tsukuba).

The change of the Fe-*K* edge in *X*-ray absorption (1 → 16 in Figure 2) corresponds to the decay in optical absorption of the blue intermediate species. The time regions of the spectra in Figure 2(a) and (b) are 5 ms—0.16 s and 50 ms—1.2 s after mixing the solutions, respectively. The Fe-*K* edge tends to shift to lower energy during the reaction. Four isosbestic points are clearly observed at 7.134, 7.155, 7.180, and 7.213 keV. The final spectrum 16 is in accordance with the spectrum of the Fe^{2+} aqua ion which was measured independently. Since XANES spectra are sensitive to the effective atomic charge of the nucleus, these reflect the change in charge of the Fe atom, $Fe^{3+} \rightarrow Fe^{+3-\delta} \rightarrow Fe^{2+}$ (Figure 2). With an increase in $[H^+]$, the overall reaction rate is considerably reduced as shown in Figure 2(c) and (d). Two possibilities exist: i, the formation of the protonated intermediate species $[(Fe^{III}–H_2Q)^{3+}{}_{aq}]^*$ increases with the increase in $[H^+]$ and/or ii, the

$$[Fe^{III}(OH_2)_6]^{3+} \rightleftharpoons [Fe^{III}(OH_2)_5OH]^{2+} + H^+ \quad (1)$$

$$[Fe^{III}–H_2Q)]^* \rightleftharpoons Fe^{II}–HQ^{\cdot} + H^+ \quad (2)$$

§ Step 1 proceeds in the time region of 10—20 ms, while steps 2 and 3 proceed 5—10 s at $[H_2Q] = 1.5 \times 10^{-3}$ mol dm^{-3}, $[Fe^{3+}] = 0.01$—0.05 mol dm^{-3}, and $[H^+] = 0.1$—0.4 mol dm^{-3}. On the other hand, in the catechol system, steps 2 and 3 are clearly distinguished from each other.

¶ The empirical rate law can be written for the electron transfer in the present system (see ref. 15):

$$A + D \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A^- + D^+$$

$$A + D^+ \xrightarrow{k_p} A^- + \text{product}$$

where A and D denote Fe^{3+} aqua ion and hydroquinone, respectively. Assuming steady-state concentrations for D^+, the following equation is derived.

$$-d[A]/dt = \{2k_p[A]/(k_b + [A^-] + k_p[A])\}k_f[A][D]$$

Under the condition $k_b[A^-] \ll k_p[A]$, this equation can be written as $-d[A]/dt = 2k_f[A][D]$. Thus, the second-order rate constant k_0 is $2k_f$. In our system,

$$-d[Fe^{III}]_{tot}/dt = \{2k_2K_1/(1 + K_h/[H^+] + K_1[H_2Q])\}[Fe^{III}]_{tot}[H_2Q].$$

The second rate constant k_0 is $2k_2K_1$. Therefore, the second step in the above scheme could not be followed. This rate law satisfies our kinetic data under dilute conditions. Detailed rate data will be reported elsewhere.

deprotonation of the intermediate species is reduced with the increase in $[H^+]$. The former case is related to the equilibrium in equation (1) and the latter to the equilibrium in equation (2). These complicated problems (proton ambiguity) are not clearly solved even by the present time-resolved *X*-ray absorption spectroscopy.

We have shown that time-resolved *X*-ray absorption spectroscopy (particularly XANES), when fully interpreted, could provide much more information on the co-ordination number, geometry, effective charge, and degree of covalency[16] in the identification of the reaction intermediates.

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References

1 R. G. Wilkins, 'Advances in Inorganic and Bioinorganic Mechanisms,' ed. A. G. Sykes, Academic Press, London, 1983, vol. 2.
2 'EXAFS Spectroscopy,' eds. B. K. Teo and D. C. Joy, Plenum Press, New York, 1981.
3 T. Matsushita, H. Oyanagi, S. Saigo, U. Kaminaga, H. Hashimoto, H. Kihara, N. Yoshida, and M. Fujimoto, *Jpn. Appl. Phys.*, 1986, **25**, L523.
4 T. Matsushita and R. P. Phizackerley, *Jpn. Appl. Phys.*, 1981, **20**, 2223.
5 R. P. Phizackerley, Z. U. Rek, G. B. Stephenson, S. D. Conradson, K. O. Hodgson, T. Matsushita, and H. Oyanagi, *J. Appl. Crystallogr.*, 1983, **16**, 220.
6 A. M. Flank, A. Fontaine, A. Jucha, M. Lemonnier, D. Raoux, and C. Williams, *Nucl. Instrum. Methods*, 1983, **208**, 651.
7 T. Matsushita, H. Oyanagi, S. Saigo, H. Kihara, and U. Kaminaga, 'EXAFS and Near Edge Structure III,' eds. K. O. Hodgson, B. Hedman, and J. E. Penner-Hahn, Springer-Verlag, 1984, 476.
8 A. Fontaine, E. Dartyge, and C. Tourillon, 'EXAFS and Near Edge Structure III,' eds. K. O. Hodgson, B. Hedman, and J. E. Penner-Hahn, Springer-Verlag, 1984, 403.
9 D. E. Sayers, D. Bazin, H. Dexpert, A. Jucha, E. Dartyge, A. Fontaine, and P. Lagarde, 'EXAFS and Near Edge Structure III,' eds. K. O. Hodgson, B. Hedman, and J. E. Penner-Hahn, Springer-Verlag, 1984, 209.
10 G. Maire, F. Garin, P. Bernhardt, P. Girard, J. L. Schmitt, E. Dartyge, H. Dexpert, A. Fontaine, A. Jucha, and P. Lagarde, *Appl. Catal.*, 1986, **26**, 305.
11 S. Saigo, H. Oyanagi, T. Matsushita, H. Hashimoto, N. Yoshida, M. Fujimoto, and T. Nagamura, *J. Phys.* 1986, **47**, C8-555.
12 J. H. Baxendale, H. R. Hardy, and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1951, **47**, 963.
13 B. S. Brunschwig, C. Creutz, D. H. Macartney, T-K. Sham, and N. Sutin, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 113.
14 A. Haim, *Acc. Chem. Res.*, 1975, **8**, 264.
15 M. Kimura and Y. Kaneko, *J. Chem. Soc., Dalton Trans.*, 1984, 341.
16 L-S. Kau, J. Spina-Solomon, J. E. Penner-Hahn, K. O. Hodgson, and E. I. Solomon, *J. Am. Chem. Soc.*, 1987, **109**, 6433.

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