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Periodate – an alternative oxidant for testing potential water oxidation catalysts

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Abstract

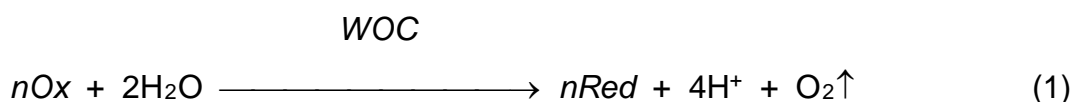
The redox catalyst ruthenium dioxide, prepared via the Adams technique, i.e. Ru(Adams), is used as a water oxidation catalyst using the oxidants (i) Ce(IV) in 0.5 M H₂SO₄ and (ii) periodate in 0.5 M H₂SO₄, water and 0.1 M KOH. Like Ce(IV), periodate is a very strong oxidant that is able to oxidise water to oxygen and can be readily monitored spectrophotometrically at 280 nm, compared with 430 nm for Ce(IV). More importantly, *unlike* Ce(IV), which is unstable towards hydrolysis above pH 1, periodate is stable in acid, water and strong alkali. A spectrophotometric study of the kinetics of periodate reduction, and concomitant oxidation of water to O₂, reveals that in the presence of a suitable redox catalyst, Ru(Adams) in this work, periodate is able to effect the stoichiometric oxidation of water, with a turnover number > 64. In just water, the kinetics of the latter reaction appear diffusion-controlled, due to the large thermodynamic driving force, a measure of which is the difference in redox potential, i.e. $\Delta E = 423$ mV. As this difference is decreased, $\Delta E = 396$ mV in acid and 290 mV in strong alkali (0.1 M KOH), the kinetics become increasingly activation-controlled and slower. These findings are discussed briefly with regard to the possible use of (i) periodate as an alternative oxidant in the rapid screening of new potential water oxidation catalyst material powders that are stable only under near neutral and/or alkaline conditions, and (ii) Ru(Adams) as a benchmark catalyst.

Keywords: Oxygen-catalysis, periodate, ruthenium dioxide, redox catalysis, Adams catalyst

1. Introduction

There has been much renewed interest in recent years in the development of efficient, long-lived, low-cost, solar-driven photosystems for the splitting of water into hydrogen and oxygen¹⁻³. One of the great challenges in creating such a system is the identification of a suitable redox catalyst to mediate the oxidation of water, the oxygen evolution reaction, *OER*, by the photogenerated oxidant, which is usually a photo-generated valance-band hole in a semiconductor photocatalyst^{4,5}. The reason for the significant interest in water oxidation catalysts, *WOCs*, rather than water reduction catalysts is that the oxidation of water is an electrochemically irreversible process, i.e. has a very low exchange current density, typically $< 10^{-5}$ mA cm⁻², whereas water reduction is normally an electrochemically reversible process with a high exchange current density on many materials⁴, i.e. typically > 0.1 mA cm⁻². Thus, even when using the most active electrocatalysts, it follows that a much greater overpotential is required to drive the former (ca. 256 mV using RuO₂) than the latter (ca. 25 mV using Pt) at a current density (20 mA cm⁻²)⁴ that is typically associated with a very efficient solar to chemical energy conversion device under an incident solar flux of 100 mW cm⁻². Obviously, the lower the overpotential for the *OER* the more efficient the overall cell, but the best *WOCs* are usually based on oxides of Ru or Ir, which are not abundant⁴. It is not surprising, therefore, that there has been a great deal of effort in recent years to identify new, alternative, inexpensive, i.e. Earth-abundant, highly active *WOCs*³.

As part of this effort, many new *WOCs* are, initially at least, generated in powder form, but their subsequent, reliable transformation into an anode and testing as an electrocatalyst for the oxidation of water is non-trivial and time-consuming⁶. It is also impractical for testing many different potential *WOCs*, which the increasingly employed combinatorial methods are very effective at producing⁷. Fortunately, a quick initial impression of the activity of a powdered *WOC* can be gleaned from its ability to mediate a redox reaction involving the oxidation of water, i.e. reaction (1).



Where *Ox* is the oxidant, *Red* is the reduced form of *Ox*, and *n* is the number of equivalents necessary to consume 4 electrons from water. Obviously, *Ox* must have

an oxidation potential greater than that of water, i.e. $E(Ox/Red) > E(O_2/H_2O)$; where the latter is equal to $1.23 - 0.059pH$. Usually, the greater the difference, ΔE , the greater the value of ΔG and the faster the process, until, that is, ΔE is so large that the rate of reaction is limited by the rate of diffusion of Ox to the surface of the WOC catalyst particles⁸.

Reaction (1) is an example of redox catalysis, the understanding of which has been greatly advanced through the significant efforts of Spiro and his collaborators^{9,10}. In particular, through an examination of over 70 different redox systems, they have demonstrated that the role of the redox catalyst is often simply that of a conductor of electrons, as illustrated in Figure 1 for the overall redox reaction, which in this case is the oxidation of water by a strong oxidant, Ox , i.e. reaction (1)^{8,9}. It follows that the kinetics observed when using a WOC in powdered form as a redox catalyst for reaction (1) are usually related directly to its eventual performance as an electrocatalyst at the anode in a solar-driven, water-splitting cell. As a consequence, as noted by many groups^{3,8}, redox catalysis based on reaction (1) has great potential as a screening tool for powder-based $WOCs$ and is becoming an increasingly popular method as such³.

In such studies^{3,8}, the WOC is commonly dispersed in solution, and upon addition (or upon electrochemical or photochemical generation) of the oxidising chemical species, Ox , the rate of reaction (1) is measured, usually spectrophotometrically via its subsequent decrease with time, at a rate which reflect the activity of the WOC . A common chemical oxidant in such work is $Ce(IV)$, where $E(Ce(IV)/Ce(III)) = 1.45 V$ in $0.5 M H_2SO_4$, but its use is restricted to highly acidic conditions because it undergoes hydrolysis above $pH 1$. In this system, the driving force for reaction (1), which is directly related to ΔG° , is $\Delta E = (E^\circ(Ce(IV)/Ce(III)) - E^\circ(O_2/H_2O)) = 220 mV$. Unfortunately, many of the current proposed 'Earth-abundant' oxygen catalysts, such as Co_3O_4 and NiO , are unstable in acidic solution and so require an oxidant that can operate at much higher pHs ^{3,4}.

If the *WOC* under test is stable and active under mildly acidic conditions, then the preferred, alternative oxidant to Ce(IV) is usually Ru(bpy)₃³⁺, since $E^\circ(\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}) = 1.26 \text{ V}$. Ru(bpy)₃³⁺ can be generated chemically (using Cl₂ or PbO₂)¹¹ or electrochemically, but, unfortunately, it is increasingly unstable with pH above pH 1^{12,13}, and so, with increasing pH, it becomes more difficult to store and use. As a result, most groups working on new *WOCs* choose to generate Ru(bpy)₃³⁺ *in situ*, via the oxidative quenching of its electronically excited state by a sacrificial electron donor such as persulfate^{14,15} or Co(II) pentammine chloride^{16,17}. Whatever the mode of Ru(bpy)₃³⁺ generation, Ru(bpy)₃³⁺ works best as the oxidant, Ox, in reaction (1) over the range pH 3–5, since much above pH 5 it degrades rapidly with little or no generation of oxygen^{12,13,18} and much below pH 3, $\Delta E (= E(\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}) - E(\text{O}_2/\text{H}_2\text{O}))$ is insufficient to drive reaction (1) at a easily measurable rate. Interestingly, even over the range pH 3–5, typical maximum yields of O₂ are usually < 70%^{12,13}, which is in stark contrast to the Ce(IV) test system where they are usually > 90% for the same proven *WOC*, such as RuO₂^{8,19,20}.

The problem of testing new *WOCs* with a redox system is exacerbated by the fact there are many reported^{3,4} very active *WOCs* that are only stable under conditions of high alkalinity (i.e. $\geq 0.1 \text{ M OH}^-$), such as Fe₂O₃-doped NiO²¹ and, more recently, Ni₂P(core)/NiO_x(shell) particles²². In order to rapidly screen all *WOCs*, regardless of their pH stability, what is required is an oxidant that is able to effect reaction (1) in the presence of an established *WOC* in acid, neutral and alkaline conditions. In this paper we report on the effective use of the two electron oxidant periodate in this role, as demonstrated using a highly reproducible, active, benchmark *WOC*, Ru(Adams), i.e. RuO₂, prepared by a slightly modified version of the Adams method²³.

Periodate has been used in the recent past to demonstrate the action of a number of different *homogeneous WOCs*²⁴⁻²⁷, but has been much less frequently used for testing *heterogeneous WOCs*^{8,27}. The particular novelty of this work is not only the use of periodate as the oxidant in testing a *heterogeneous WOC*, but also, and more importantly, its use to assess its underlying activity via the spectrophotometric

monitoring of the decay of the periodate to iodate, under conditions in which the oxidant is repeatedly in vast excess compared to the catalyst.

2. Experimental

All chemicals used were purchased from the Sigma-Aldrich Chemical Company. Doubly distilled and deionised water was used throughout. The 0.1 M Ce(IV) solution in sulphuric acid was used as received. The 0.1 M NaIO₄ solution was freshly prepared on the day of the kinetic run or O₂ evolution test. Powder XRD spectra of the Ru(Adams) catalyst were recorded using a Panalytical X'pert powder X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ nm) at 40 kV and 40 mA with a step size of 0.02°.

2.1 Preparation of Ru(Adams)

In the slightly modified preparation of Ru-Adams²³, 0.5 g RuCl₃.xH₂O and 10 g NaNO₃ were dissolved in 15 mL water. The resulting solution was placed in a crucible and heated at 500°C for 25 min in a muffle furnace. The obtained melt was then allowed to cool before 80 mL of water were added to dissolve the NaNO₃ in the Ru(Adams)/NaNO₃ cake. The black, finely divided, Ru-Adams catalyst powder was then filtered off, washed thoroughly with water, and dried in air. Figure 2 illustrates a typical XRD powder pattern recorded for the Ru(Adams) powder, along with that reported in the literature²⁸ for RuO₂, which was used to confirm its identity. N₂ BET analysis of the powder, carried out using a Micromeritics Tristar 3020, revealed a specific surface area of ca. 150 m² g⁻¹. A typical dispersion of the Ru(Adams) was prepared by adding 3 mg of the Ru(Adams) to 50 mL of the aqueous solution under test (i.e. 0.5 M H₂SO₄, water or 0.1 M KOH, for work carried out under acidic, neutral and alkaline conditions, respectively). The suspension was subjected to ultrasound using an ultrasonic bath (Grant XUBA3) for 15 min and then stirred overnight to create a very stable dispersion that exhibited a typical background absorption (ΔAbs_{800}) of 0.12 at 800 nm.

2.2 Monitoring the kinetics of photocatalysis

In a typical experiment, 2.5 mL of the 60 mg L⁻¹ Ru(Adams) catalyst were placed in a quartz cuvette, which was in turn placed in a UV/Visible spectrophotometer (Perkin Elmer Lambda 35). The removable sample holder plate of the latter instrument was replaced with a magnetic stirrer to allow for the continuous (ca. 800 rpm) stirring of the cuvette's contents. The absorbance of the dispersion was monitored at a wavelength that was suitable for monitoring the concentration of the oxidant under test (430 nm for Ce(IV) and 280 nm for periodate) as function of time. After 5 min of monitoring the absorbance, the redox catalytic reaction was initiated by the injection of 90 μL of a 0.1 M solution of the oxidant under test. The decay of the oxidant was continuously monitored spectrophotometrically until no further, significant decay in absorbance was observed and the reaction was deemed complete. In all cases, i.e. whatever the oxidant and pH, no decay of the oxidant was observed over the time course of the kinetic runs in the absence of the Ru(Adams) catalyst.

2.3 Monitoring the generation of oxygen

The evolution of oxygen arising from reaction (1) was monitored manometrically using a 125 mL Drechsel bottle equipped with a pressure transducer sealed in its top, and a rubber septum side injection port which allowed the introduction of the *WOC* catalyst, here a 2.5 mL dispersion of 12 mg of Ru(Adams), into 100 mL of a 3.6 mM solution of the oxidant under test⁸. Upon addition of the catalyst dispersion to the sealed Drechsel bottle, the pressure change in the head space was monitored as a function of time until no further increase in pressure due to gas evolution was observed. At this point the overall change in pressure due to gas evolution was measured and used to calculate the number of moles of O₂ generated. In other work, for each of the Drechsel-based, gas-generating runs conducted at different pH, the identity and level of O₂ generated was confirmed by gas chromatography using a Shimadzu GC-2014 instrument equipped with a thermal conductivity detector (TCD) operated at 140°C and an 1.8 m-long Alltech CTR-1 column heated to 32°C, with a 65 mL min⁻¹ flow of Ar as the carrier gas.

3. Results and Discussion

3.1 Ce(IV) in acid

As noted earlier, a past common route to assessing the activity of a powdered potential WOC, if stable under acidic conditions, would be to disperse it into 2.5 mL of 0.5 M H₂SO₄ (60 mg L⁻¹, here) and monitor the kinetics of Ce(IV) decay caused by reaction (1) spectrophotometrically, after the injection of 90 μL of 0.1M Ce(IV) in 0.5 M H₂SO₄ into the catalyst dispersion. Previous work carried out by this group has established that one of the best WOCs for reaction (1) is Ru(Adams)²³. In this work, the preparation of Ru(Adams) has been modified slightly compared to that reported earlier, so as to generate a more reproducible, higher surface area (150 m² g⁻¹ compared to 113 m² g⁻¹)²³ WOC. This material is ideal for testing out other potential oxidants that offer an alternative to Ce(IV), such as periodate, at any pH. Ru(Adams) also appears to be a suitable benchmark material with which to compare the performance of other, powdered, alternative new WOCs.

Figure 3 illustrates the typical observed change in the spectrum of the Ce(IV)/Ru(Adams) system as a function of time upon the first injection of Ce(IV) solution into a dispersion of Ru(Adams). As can be seen from the data in figure 3, the dispersion of Ru(Adams) – a black powdered WOC, spectrophotometrically simply provides a grey background, and so constant absorbance, at all wavelengths, as the Ce(IV) concentration, [Ce(IV)], decays due to reaction (1). As a consequence, this allows the decay in [Ce(IV)] due to reaction (1) to be monitored spectrophotometrically, and so the kinetics of water oxidation to be measured. The wavelength used for this purpose, 430 nm, is highlighted in figure 3 by the vertical broken red line. The insert diagram illustrates the measured variation in absorbance at 430 nm of the same 60 mg L⁻¹ dispersion of Ru(Adams) for a series of repeat injections of Ce(IV), in which the three observed decay profiles are due solely to the changes in [Ce(IV)] caused by reaction (1).

The decay profiles illustrated in figure 3 are easily recorded and provide a great deal of useful information. For example, if no decay in Ce(IV) absorbance is observed then it would appear that the powdered potential WOC under test is not a promising WOC,

most likely because it has an high over-potential for water oxidation. However, little or no observed *WOC* activity may also be observed if the *WOC* under test forms a poor dispersion, as is often the case for highly crystalline materials with low ($< 10 \text{ m}^2 \text{ g}^{-1}$) specific surface areas^{8,29}. Obviously, one way to attempt to address such a problem would be to use a much higher concentration of the *WOC*.

Clearly, for the best results, the *WOC* under test has to be well-dispersed, and a quick and useful method to assess quickly, albeit crudely, the extent and stability of the *WOC* dispersion is to monitor its absorbance at a wavelength where the oxidant does not absorb, say 800 nm ^{30,31}. Ideally, for a well dispersed powder such as Ru(Adams), the absorbance due to the catalyst dispersion, ΔAbs_{800} , should be > 0.1 (for Ru(Adams) it is typically ca. 0.12) and should not change during the course of a kinetic run. If, for any potential *WOC* catalyst under test, the value of ΔAbs_{800} is found to be much less than 0.1, then the powder is poorly dispersed and the potential *WOC* is unlikely to exhibit much, if any, activity. Under such circumstances, a higher concentration of catalyst is likely to be needed, or the aggregated particles may need to be broken up more, through ball-milling or the use of ultrasound. The variation in ΔAbs_{800} over the time course of a kinetic run can also be very informative. For example, if, as often happens for some metal oxides such as MnO_2 , the value of ΔAbs_{800} drops significantly, then this is may be taken as evidence of catalyst particle aggregation and precipitation, i.e. the powdered *WOC* dispersion is not sufficiently stable. In many such instances, the initial degree of aggregation and the tendency of the *WOC* particles to aggregate can be improved greatly though the use of an inert anti-flocculating agent, such as silica³².

From the decay profiles illustrated in figure 3, for the Ce(IV)/Ru(Adams) *Ox/WOC* system, it appears that: (i) Ru(Adams) is effective in mediating reaction (1), when *Ox* = Ce(IV) and (ii) the catalyst dispersion is stable over the time course of the three injections. Recording the decay profiles over at least 3 injections of oxidant is useful as it reveals whether the *WOC* remains consistently active or not with repeated use. For example, if, upon injection, [Ce(IV)] is found to decay a little and then stop or slow

down considerably, this would suggest that the *WOC* has been quickly rendered inactive and/or subject to anodic corrosion. Interestingly, the latter effect will also usually manifest itself by a significant drop in the initial value of ΔAbs_{800} upon the initial injection of the oxidant. Indeed, this is observed when highly hydrated RuO_2 , i.e. $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, is used in the $\text{Ce(IV)}/\text{WOC}$ test system, since the latter is more readily oxidised to RuO_4 by the Ce(IV) than able to mediate reaction (1)³³. Only upon heat-treating the $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (thermal activation) is it rendered stable and active as a *WOC*³⁴.

A closer inspection of the decay profiles illustrated in figure 3 reveals that the rate of decay of $[\text{Ce(IV)}]$ decreases with each injection. Indeed, an analysis of each of the three decays in $[\text{Ce(IV)}]$ illustrated in figure 3 on the basis of first order kinetics over one half-life yields increasing values for the first order rate constant, k_1 , as shown in Table 1. Table 1 also contains the values of the first order decay fit correlation coefficients (R^2) and the initial values of ΔAbs_{800} obtained for the three decays illustrated in figure 3. Previous work conducted on this system has shown that this apparent decay in activity is actually due to the accumulation of Ce(III) , which lowers the redox potential of the $\text{Ce(IV)}/\text{Ce(III)}$ couple, as predicted by the Nernst equation, which in turn reduces the value of ΔE to such an extent as to adversely affect the kinetics of reaction (1)³⁵. These previous studies have shown that it is possible to fit the observed kinetics of decay exhibited by the Ru(Adams) , for all three injections and more, to those predicted by an electrochemical model based on the Nernstian highly reversible reduction of Ce(IV) coupled to the irreversible oxidation of water³⁵. However, such an analysis is quite involved and unnecessary here, given that the purpose of the test systems under study is to provide a quick and simple assessment of the *WOC* activity of the powdered material under test. As a consequence, here we focus on just the first of the three values of k_1 given in Table 1 for the Ce(IV) system, i.e. that for the 1st injection, since it is associated with the kinetics of reaction (1) which are least affected by the level of Ce(III) present and which, from previous studies³⁵, is near to that expected if the rate of reaction were controlled by the diffusion of the Ce(IV) ions to the surface of the Ru(Adams) particles. As such, this value of k_1 (ca.

0.33 min⁻¹, see Table 1) is not so much a measure of the fundamental WOC activity of Ru(Adams) but more a measure of the effective surface area of the aggregated dispersed particles^{19,20}. It follows that, when using another oxidant, such as periodate at any pH, rather than Ce(IV) in acid, with the same catalyst, which presumably disperses to the same or similar extent (as crudely assessed by the value of ΔAbs_{800} (= ca. 0.12 for the Ce(IV) system)), then, if the measured value of k_1 is $\ll 0.33 \text{ min}^{-1}$, the reaction is probably activation- rather than diffusion-controlled^{19,20}.

The Ce(IV)/Ce(III) redox system is a well-known reversible redox system³⁶ and so the redox potential, i.e. the mixture potential, E_{mix} , it imposes on the Ru(Adams) particles will reflect the ratio of Ce(IV) to Ce(III) at the surface of the catalyst particles, via the Nernst equation. In the electrochemical model of redox catalysis, at E_{mix} , the rate of oxidation of water (the anodic current) on a catalyst particle is equal to the rate of reduction of Ce(IV), the cathodic current³⁵. In such a system, if ΔE is sufficiently large, and [Ce(III)] small, as in the 1st injection in figure 3, then the rate of reaction is limited by the rate of diffusion of the Ce(IV) ions to the redox catalyst particles. A schematic illustration of current-voltage curves associated with this coupling of the two redox systems via a redox catalyst is given in figure 4³⁵.

The first-order rate constant, k_D (units: s⁻¹), for a diffusion-controlled reaction between the Ce(IV) ions and an aggregated Ru(Adams) particle can be calculated using a modified version of the Smoluchowski equation³⁷,

$$k_D = 12D[\text{Ru(Adams)}]/(1000\rho d^2) \quad (2)$$

where D is the diffusion coefficient of the Ce(IV) ions (assumed³⁷ to be $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), [Ru(Adams)] is the concentration of catalyst (0.06 g L^{-1}), ρ is the density of the aggregated RuO₂ particle (assumed to be that of bulk RuO₂ itself, 6.97 g cm^{-3}) and d is the average diameter of the aggregated catalyst particles (cm). A value for the aggregated Ru(Adams) particles of $4.3 \mu\text{m}$ can be calculated using eqn (2) based on a k_1 value of 0.33 min^{-1} , i.e. $5.5 \times 10^{-3} \text{ s}^{-1}$. This value compares favourably to that of $11 \pm 6 \mu\text{m}$ measured using optical microscopy¹⁹ for a similar dispersion of RuO₂, given that the calculation of d via eqn (2) is based on the assumption that the density of the

aggregated Ru(Adams) particles is that of bulk RuO₂, when in fact it will be much less, and so the value of d will be much greater than 4.3 μm , as is found.

In the Ce(IV)/Ru(Adams) system, the three serial decay profiles, each one largely to completion, illustrated in figure 3, coupled with the fact that after each injection the number of moles of initial oxidant (9.0 μmoles) is in vast excess to that of WOC present (1.1 μmoles), help establish the redox catalyst credentials of the Ru(Adams) in terms of turnover number; TN , defined here as the ratio of number of moles of oxidising equivalents consumed to number of moles of catalyst used. From the data in figure 3, the value of TN appears to be > 32 . For any potential new WOC, a value > 4 is essential, but the greater the value above 4, the more reassuring it is that the catalyst is stable, active and deserving of the sobriquet 'WOC'. Clearly, no material can be claimed to be a WOC, although some have³⁸, if the amount of redox catalyst used is in vast excess compared to the oxidant present.

Finally, no claim of WOC activity would be complete without establishing that the decay of Ox in reaction (1) is accompanied by the generation of **stoichiometric** amounts of O₂. The latter is established here using the manometric system described earlier, in which a 2.5 mL dispersion of 12 mg of Ru(Adams) is injected into 100 mL of a 3.6 mM solution of the oxidant under test, in a sealed system, and any subsequent gas evolution monitored by the increase in internal pressure. Using this system, the pressure change was recorded as a function of time after injection for Ox = Ce(IV), and the results are illustrated in figure 5. From this data, and knowledge that: (i) a 2 mL injection of air into the same, sealed system produced a change in pressure of 26 mbar, and (ii) the overall change in pressure recorded in figure 5 is 26.2 mbar, then the number of moles of gas liberated was calculated to be 82.3 μmoles . As noted in the experimental section, additional experiments conducted using GC confirmed that the gas evolved was O₂ and confirmed the total number of moles of O₂ liberated as determined manometrically. Given that in this experiment 360 μmoles of Ce(IV) were consumed, and so 90 μmoles of O₂ should have been generated, it follows that, for the Ce(IV)/Ru(Adams) system, the %O₂ yield for reaction (1) is 91%. Further work

revealed no evidence of catalyst corrosion (due to RuO_4 formation, for example), and, as a consequence, the observed decays of Ce(IV) in figure 3 are attributed to the catalysed oxidation of water via reaction (1), mediated by the Ru(Adams) catalyst.

3.2 Periodate in acid

Under the acidic conditions used here, i.e. 0.5 M H_2SO_4 , periodate exists as periodic acid, H_5IO_6 ($\text{pK}_a = 3.29$)³⁹ and has a redox potential ($E^\circ(\text{H}_5\text{IO}_6/\text{HIO}_3) = 1.626 \text{ V}$)⁴⁰ that yields a value for $\Delta E = 396 \text{ mV}$, which is much greater than that for the Ce(IV)/Ce(III) couple in sulphuric acid ($\Delta E = 220 \text{ mV}$)³⁶, *vide infra*. Using the standard kinetic system described earlier, a series of UV/Vis spectra were recorded as a function of time upon injection of 90 μL of a 0.1 M solution of sodium periodate into 2.5 mL of the 60 mg L^{-1} Ru(Adams) catalyst in 0.5 M H_2SO_4 , and are illustrated in figure 6. The results show that $[\text{H}_5\text{IO}_6]$ decays as a function of time and can be monitored spectrophotometrically at a wavelength of 280 nm, which is highlighted by the broken red line in figure 6. The results for three sequential injections of H_5IO_6 into the same, standard dispersion of Ru(Adams) are illustrated by the decay profiles in the insert diagram in figure 6.

A first order analysis of each of these decays over two half-lives reveals the kinetics of each decay to be similar and of good first order, with values for k_1 given in table 1 and an average value for k_1 of 0.09 min^{-1} . Unlike the Ce(IV) system, there is no evidence that the reduced form of periodate, i.e. iodate, impedes the kinetics of reduction of the periodic acid, and this appears true for all pHs studied. Since the rates of decay for the three profiles are similar and reasonably first order, this initially suggests that the kinetics might be diffusion-controlled. However, because the values for k_1 (for example = 0.094 min^{-1} for the first injection for periodic acid, see Table 1) are much less than that measured for the Ce(IV) system (0.33 min^{-1}), which is for a diffusion-controlled reaction, and the values for ΔAbs_{800} are necessarily similar (ca. 0.12) for both systems, it follows that the kinetics for reaction (1) in acid where $\text{Ox} = \text{H}_5\text{IO}_6$ are not wholly diffusion-controlled, but rather are most likely largely activation-controlled.

The lack of diffusion-controlled kinetics for the $\text{H}_5\text{IO}_6/\text{Ru}(\text{Adams})$ version of reaction (1) may appear surprising at first, given that $\Delta E = 396 \text{ mV}$ compared with 220 mV when $\text{Ox} = \text{H}_5\text{IO}_6$ and $\text{Ce}(\text{IV})$, respectively. However, because of the irreversible nature of the $\text{H}_5\text{IO}_6/\text{HIO}_3$ redox couple, its clear thermodynamic advantage over the $\text{Ce}(\text{IV})$ system is largely lost as a significant overpotential is required to effect the reduction of the periodic acid on the surface of the $\text{Ru}(\text{Adams})$ catalyst particles. As a consequence, despite the large value for ΔE for the $\text{H}_5\text{IO}_6/\text{HIO}_3$ system, the observed kinetics are activation and not diffusion-controlled and the kinetics are not affected by the iodate generated. Figure 4 provides a schematic illustration of this situation, in which the irreversible reduction of an oxidant, Ox_2 , is coupled to the oxidation of water via a redox catalyst, so that the mixture current flowing through the particles is less than that expected for a diffusion-controlled process, despite the very large value for ΔE , as is the case for reaction (1) when $\text{Ox} = \text{H}_5\text{IO}_6$. Note that if the value of $E(\text{Ox}_2/\text{Red}_2)$ could be increased, then ΔE would be increased and the observed rate of reaction would also be increased, and if this increase was sufficient, then diffusion-controlled kinetics would be observed. Similarly, if ΔE were decreased then the observed rate would be greatly reduced and the kinetics would become much more obviously activation-controlled. The relevance of the latter observations becomes apparent when the observed kinetics of reaction (1) with periodate as the oxidant in water and alkali are considered.

As before, the amount of gas evolved via reaction (1) with, this time, $\text{Ox} = \text{H}_5\text{IO}_6$, was measured using the manometric system, and the results are illustrated in figure 5. From this data it can be gleaned that the overall change in pressure recorded was 59.2 mbar , and so $173 \mu\text{moles}$ of O_2 were liberated. Given that, in this experiment, $360 \mu\text{moles}$ of H_5IO_6 were consumed via reaction (1) and so $180 \mu\text{moles}$ of O_2 should have been generated, it follows that for this $\text{H}_5\text{IO}_6/\text{Ru}(\text{Adams})$ system the $\% \text{O}_2$ yield for reaction (1) is 96% . As a consequence, the observed decays of H_5IO_6 illustrated in figure 6 are attributed to the catalysed oxidation of water via reaction (1), mediated by the $\text{Ru}(\text{Adams})$ catalyst, with $\text{Ox} = \text{H}_5\text{IO}_6$. Given that periodic acid is a $2e^-$ oxidant, and generates near stoichiometric amounts of O_2 in three successive injections (figure

5 and 6) it follows that the turnover for reaction (1) in acid, where Ox = periodic acid, is > 64 , as also appears to be the case in water and strong alkali, *vide infra*.

3.3 Periodate in water and strong alkali

The pH of a typical 60 mg L^{-1} dispersion of Ru(Adams) in water is ca. pH 6, and at this pH periodate exists in its metaperiodate form^{39,40}, i.e. as IO_4^- , since the pK_a of H_5IO_6 is 3 and $K = 29$ for the equilibrium between H_4IO_6^- and IO_4^- ³⁹. At pH 6, $E(\text{IO}_4^-/\text{IO}_3^-) = 1.298 \text{ V}$ ⁴⁰ and $E(\text{O}_2/\text{H}_2\text{O}) = 0.875 \text{ V}$, so that $\Delta E = 423 \text{ mV}$, i.e. greater than that for periodate in acid. Using otherwise the same conditions as used in the study of reaction (1) in acid (see section 3.2), the kinetics of reaction (1) with $\text{Ox} = \text{IO}_4^-$ were studied spectrophotometrically via a sequence of three $90 \mu\text{L}$ injections of a 0.1 M NaIO_4 solution into 2.5 mL of an aqueous dispersion of Ru(Adams). The resulting 3 decay profiles are illustrated in figure 7(a), and each provide excellent fits to first order kinetics over two half-lives, yielding the k_1 and r^2 values given in Table 1. The former are a little bigger than the benchmark value of 0.33 min^{-1} found for Ce(IV) and previously associated with diffusion-controlled kinetics. However, this slight increase may be due, in part at least, to the Ru(Adams) forming a better dispersion in water than in acid, since: $\Delta\text{Abs}_{800} = \text{ca. } 0.14$ for the 1st injection in water compared with 0.12 in acid with Ce(IV). As a consequence, given the excellent first order nature of the kinetics and comparable value for k_1 to that for the Ce(IV) in acid system, it is very likely that in water the kinetics of reaction (1) with $\text{Ox} = \text{IO}_4^-$ are diffusion-controlled. This is not too improbable, given that a small shift in ΔE (in this case from 396 to 423 mV) can bring about a striking change in electrochemical kinetics, in this case from activation to diffusion control, as illustrated in figure 4. A manometric study revealed an $\% \text{O}_2$ yield of 92% , confirming that the reaction under study in water was reaction (1), with $\text{Ox} = \text{IO}_4^-$.

In strong alkali, i.e. 0.1 M KOH , periodate exists as $\text{H}_3\text{IO}_6^{2-}$ and although this species has a tendency to dimerise⁴¹, the dimerisation constant is not particularly large (ca. 142 M^{-1})⁴¹ and the final concentration used in this work is low ($3.6 \times 10^{-3} \text{ M}$), so $\text{H}_3\text{IO}_6^{2-}$ can be taken to be the major species present. At pH 13, $E(\text{H}_3\text{IO}_6^{2-}/\text{IO}_3^-) = 0.686 \text{ V}$ ³⁹,

and $E(\text{O}_2/\text{H}_2\text{O}) = 0.462$, so $\Delta E = 224$ mV, i.e. much less than that for periodate in acid (396 mV). As a consequence, it is not too surprising that the decays of $\text{H}_3\text{IO}_6^{2-}$ via reaction (1), as monitored spectrophotometrically under otherwise the same conditions as before, although very similar from run to run, were also very slow, and much slower than observed at the other two pHs studied. For example, in alkali the value for k_1 for the first injection was found to be ca. 0.021 min^{-1} , whereas in water it was ca. 23 times bigger (0.489 min^{-1}). This considerable decrease in apparent catalytic activity is attributed to the much lower thermodynamic driving force, as measured by ΔE , when reaction (1) is carried out in alkali (pH 13) compared with in water (pH 6). Once again a manometric study revealed an $\% \text{O}_2$ yield of ca. 96%, confirming that under very alkaline conditions the reaction under study was reaction (1) when $\text{Ox} = \text{H}_3\text{IO}_6^{2-}$.

4. Conclusions

Ru(Adams) is able to act as a WOC in mediating reaction (1) using as Ox either: (i) Ce(IV) in 0.5 M H_2SO_4 or (ii) periodate in 0.5 M H_2SO_4 , water and 0.1 M KOH. The use of periodate, in contrast to Ce(IV), as the oxidant allows the WOC activity of a wide range of materials that are not stable in acid, such as Fe_2O_3 -doped NiO, Co_3O_4 and, more recently, $\text{Ni}_2\text{P}(\text{core})/\text{NiO}(\text{shell})$ to be quickly assessed for WOC activity in water or aqueous alkali in powder form. The use of periodate in water for testing WOC activity appears particularly promising, given that the electrochemical driving force, ΔE , is sufficiently large (423 mV) that the kinetics are controlled by the rate of diffusion of the periodate ions to the surface of the Ru(Adams) catalyst particles. Although most alternatives to PGM oxide WOCs will exhibit a higher overpotential for water oxidation than Ru(Adams), a value of $\Delta E = 423$ mV in water may be sufficient to use periodate as Ox in reaction (1) for demonstrating their WOC activity, although this likely higher overpotential means that the observed kinetics are similarly less likely to be diffusion-controlled. In contrast, under alkaline conditions, ΔE is only 224 mV and so only very active WOCs with very low overpotentials for water oxidation, as found for Ru(Adams) and the oxides of Ru and Ir in general, will be able to mediate reaction (1) so as to effect an easy to measure rate of decay in $[\text{H}_3\text{IO}_6^{2-}]$. Interestingly, the

Ni₂P(core)/NiO(shell) particles reported recently by Hu and his co-workers claim an overpotential in KOH, of 290 mV for 10 mA cm⁻², which is lower than that exhibited by commercially used IrO₂ anodes. This observation suggests that such particles might well be able to effect reaction (1) in 0.1 M KOH when Ox = H₃IO₆²⁻. The above findings should prove useful to the many groups investigating new WOCs and requiring a rapid screening method that is suitable for testing materials that are stable only under near neutral and/or alkaline conditions.

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Tables

Table 1 First order rate constants calculated over 1 half-life for the cerium system, and 2 half-lives for the periodate system.

	Injection	k/ min^{-1}	$t_{1/2}/ \text{min}^{-1}$	r^2	$\Delta\text{Abs}_{800}\dagger$ (before injection)
Cerium System (over 1 half-life)					
0.5 M H₂SO₄	1	0.326	2.13	0.9938	0.116
	2	0.131	5.29	0.9874	0.0968
	3	0.0589	11.8	0.9884	0.0785
Periodate System (over 2 half-lives)					
0.5 M H₂SO₄	1	0.0938	7.39	0.9965	0.126
	2	0.0919	7.54	0.9985	0.144
	3	0.0781	8.87	0.9992	0.162
Water	1	0.489	1.42	0.9999	0.140
	2	0.354	1.96	0.9998	0.258
	3	0.296	2.34	0.9999	0.315
0.1 M KOH	1	0.0205	33.9	0.9880	0.209
	2	0.0212	32.8	0.9962	0.138
	3	0.0198	35.1	0.9981	0.137

$\dagger\text{Abs}_{800}$ (quartz cuvette + water) = 0.0442

Figure Captions

- (1) Schematic illustration of the electron transfer processes associated with the oxidation of water by an oxidant, Ox , mediated by a particle of a *WOC*.
- (2) XRD of Ru(Adams) (blue line) recorded using a PANalytical X-ray powder diffractometer. The solid black lines represent the relative peak intensities of rutile phase RuO_2 obtained from the Inorganic Crystal Structure Database (ICSD #108861)²⁸.
- (3) UV/Vis absorption spectral changes, recorded every 1 min, as a function of time after injection of 90 μL of 0.1 M Ce(IV) solution into stirred 2.5 mL dispersion of Ru(Adams) (60 mg L^{-1}) in 0.5 M H_2SO_4 contained in a 1 cm cuvette; the red vertical broken line highlights the wavelength used to monitor the kinetics of [Ce(IV)] decay, i.e. 430 nm. The insert diagram illustrates the observed decays in absorbance, monitored at 430 nm, of the same system as a function of time for 3 serial injections of 90 μL of 0.1 M Ce(IV) solution into the 1 cm cuvette containing the dispersion of Ru(Adams) in 0.5 M HNO_3 .
- (4) Schematic illustration of the current-voltage curves associated with the coupling, via redox catalysis, of the irreversible oxidation of water (solid line) to (i) the reversible (Nernstian) cathodic reduction of Ce(IV) (solid line) and (ii) the irreversible reduction of a different oxidant, Ox_2 (broken line). Note in both cases the redox catalyst particles will adopt a mixture potential so that the rate of oxidation of the water (the anodic current) is equal to the rate of reduction of the oxidant, i.e. Ce(IV) or Ox_2 (the cathodic current); both illustrated by broken vertical lines.
- (5) Plot of the recorded change in pressure, as measured using the digital manometer in the system, following the injection (solid line) of a 2.5 mL dispersion of 10 mg of Ru(Adams) into 100 mL of a 3.6 mM Ce(IV) solution in 0.5 M H_2SO_4 ; total change in pressure = 26.2 mbar. The broken line illustrates the change in pressure versus time recorded under the same conditions as above, i.e. under acidic conditions, but using $NaIO_4$ as the oxidant; total change in pressure = 56.5 mbar.
- (6) UV/Vis absorption spectral changes, recorded every 1 min, as a function of time after injection of 90 μL of 0.1 M $NaIO_4$ solution into a stirred 2.5 mL dispersion of Ru(Adams), 60 mg L^{-1} , in 0.5 M H_2SO_4 contained in a 1 cm cuvette; the red vertical

broken line highlights the wavelength used to monitor the kinetics of $[H_5IO_6]$ decay, i.e. 280 nm. The insert diagram illustrates the observed decays in absorbance, monitored at 280 nm, of the same system as a function of time for 3 serial injections of 90 μL of 0.1 M NaIO_4 solution into the 1 cm cuvette containing the dispersion of Ru(Adams) in 0.5 M H_2SO_4 .

(7) Absorbance (measured at 280 nm) versus decay time for 3 repeat injections of 90 μL 0.1 M NaIO_4 into a 1 cm quartz cuvette containing a 2.5 mL dispersion of Ru-Adams (60 mg L^{-1}) in **(a)** water, and **(b)** 0.1 M KOH.

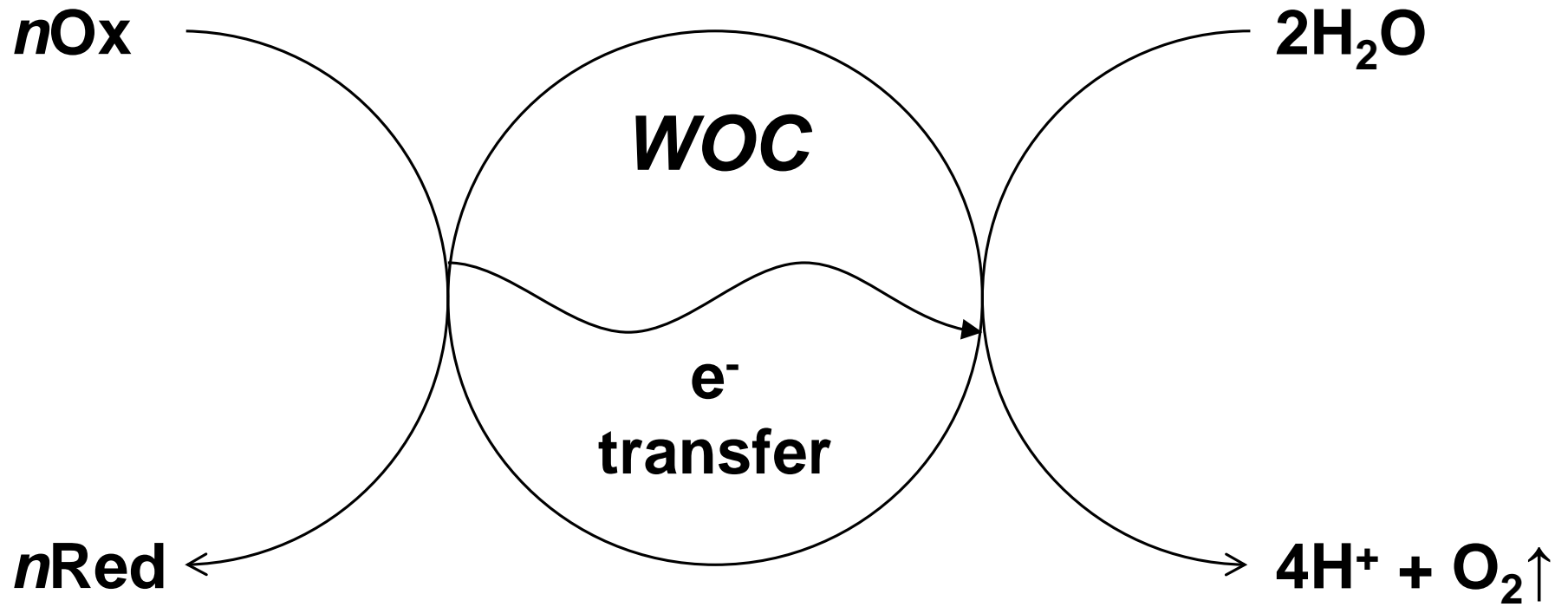


Figure 1

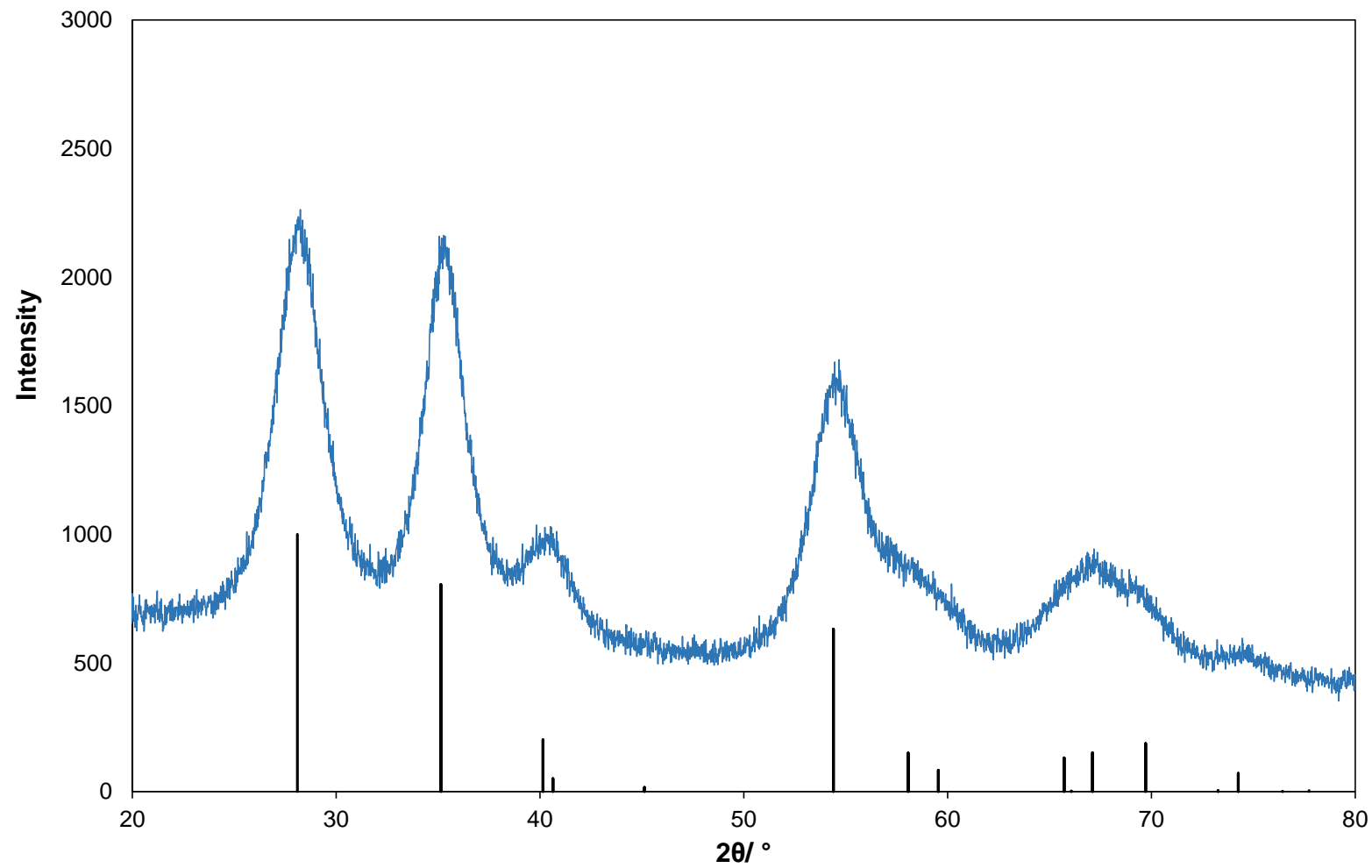


Figure 2

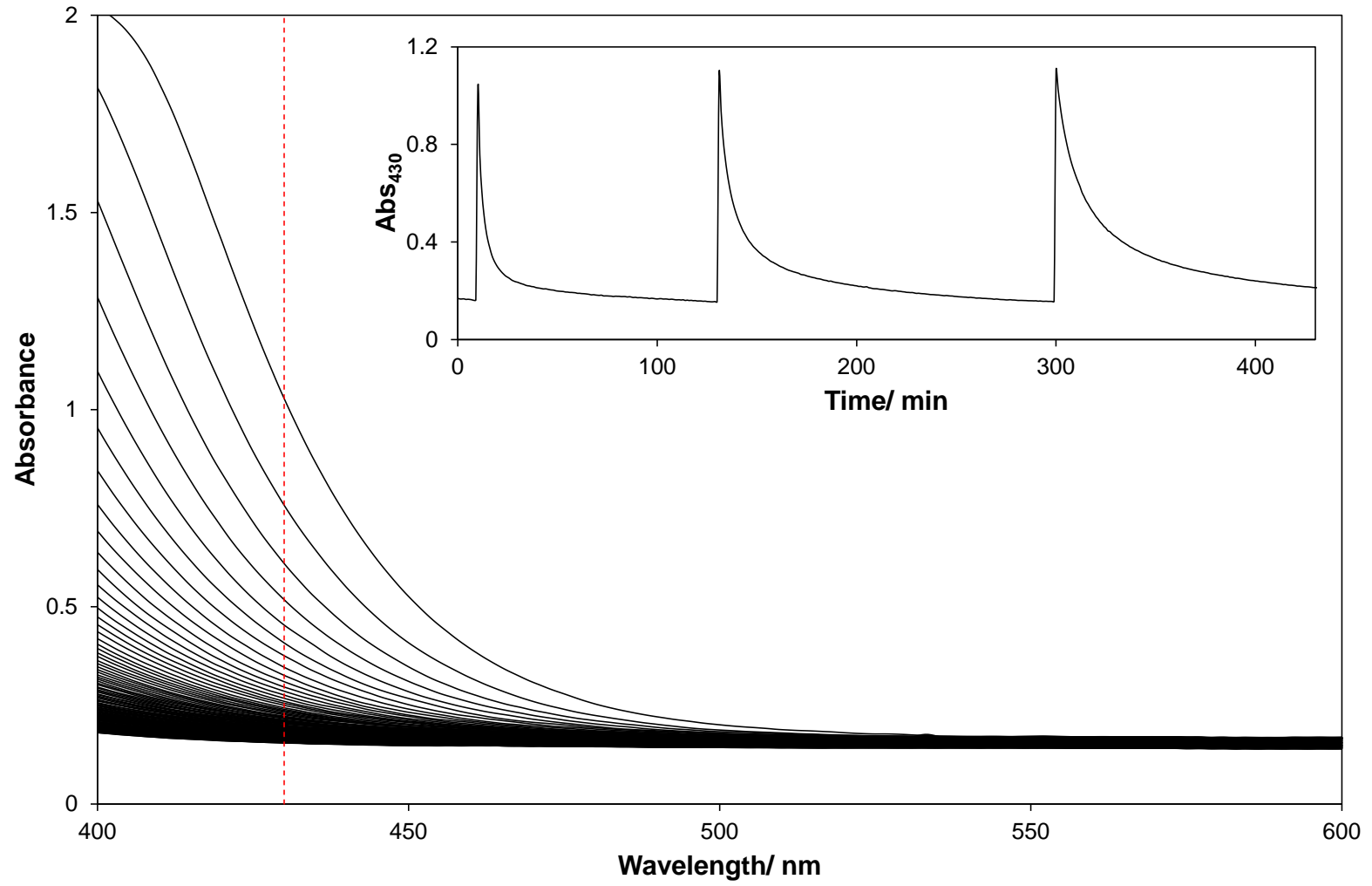


Figure 3

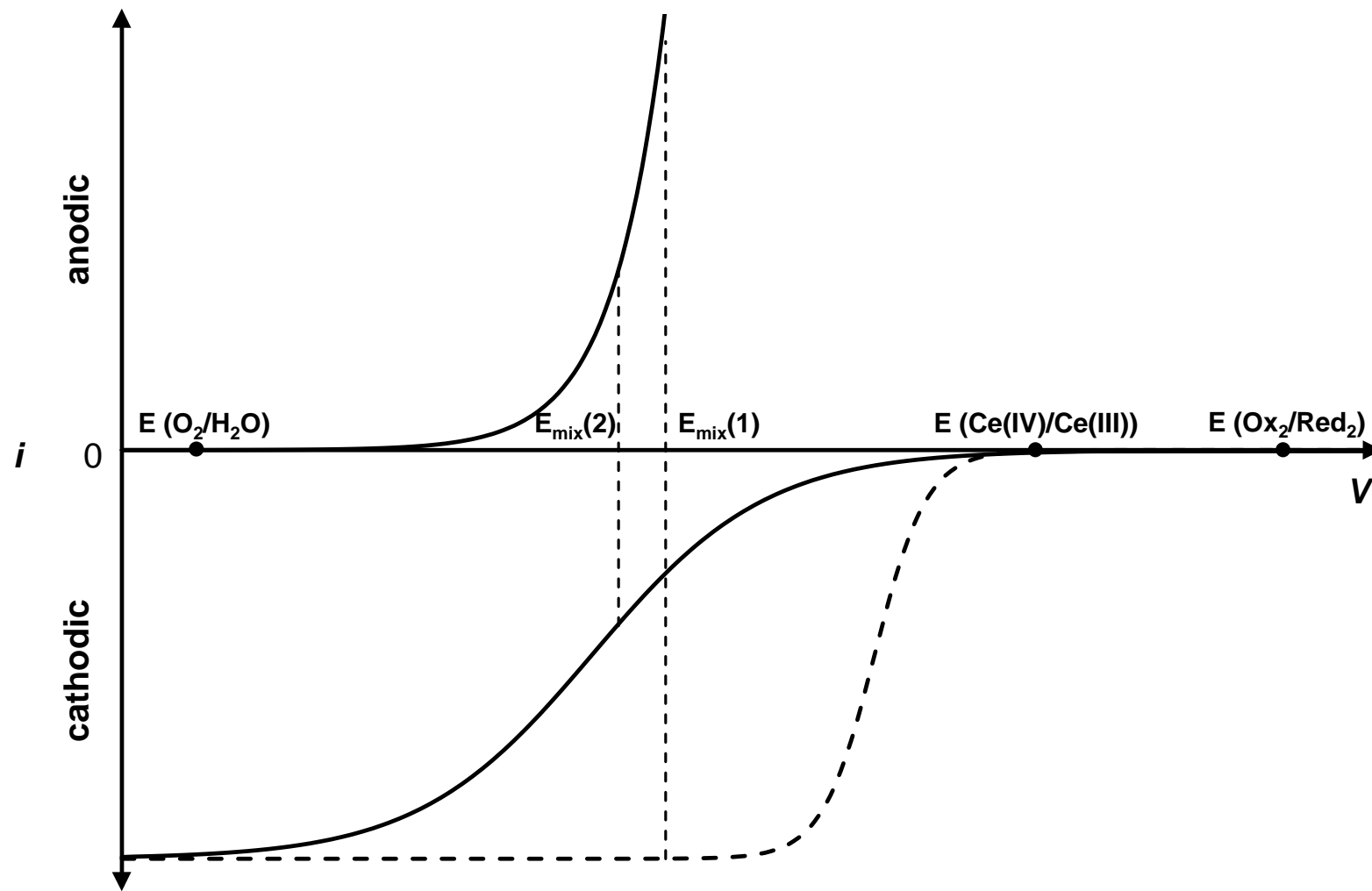


Figure 4

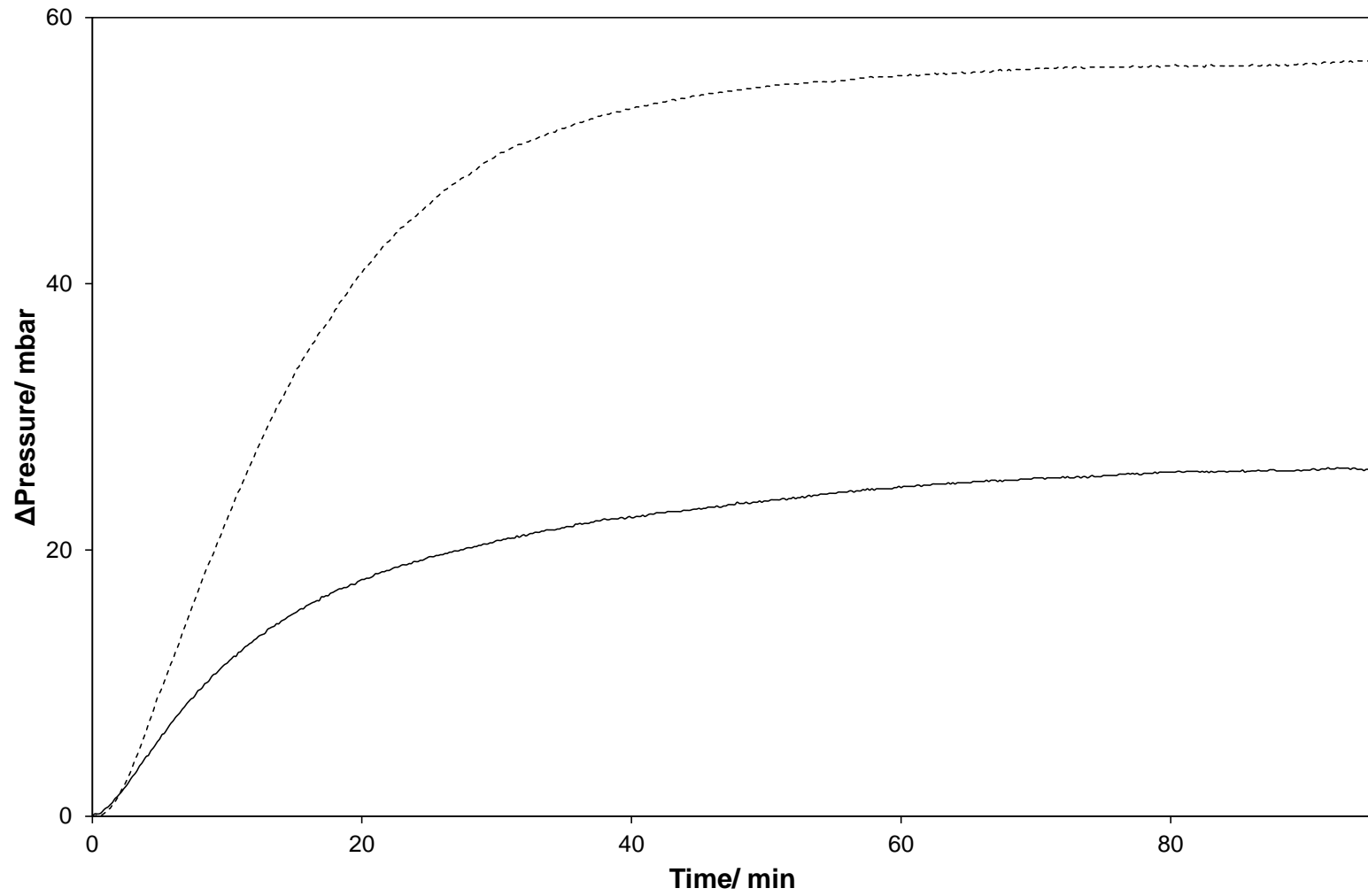


Figure 5

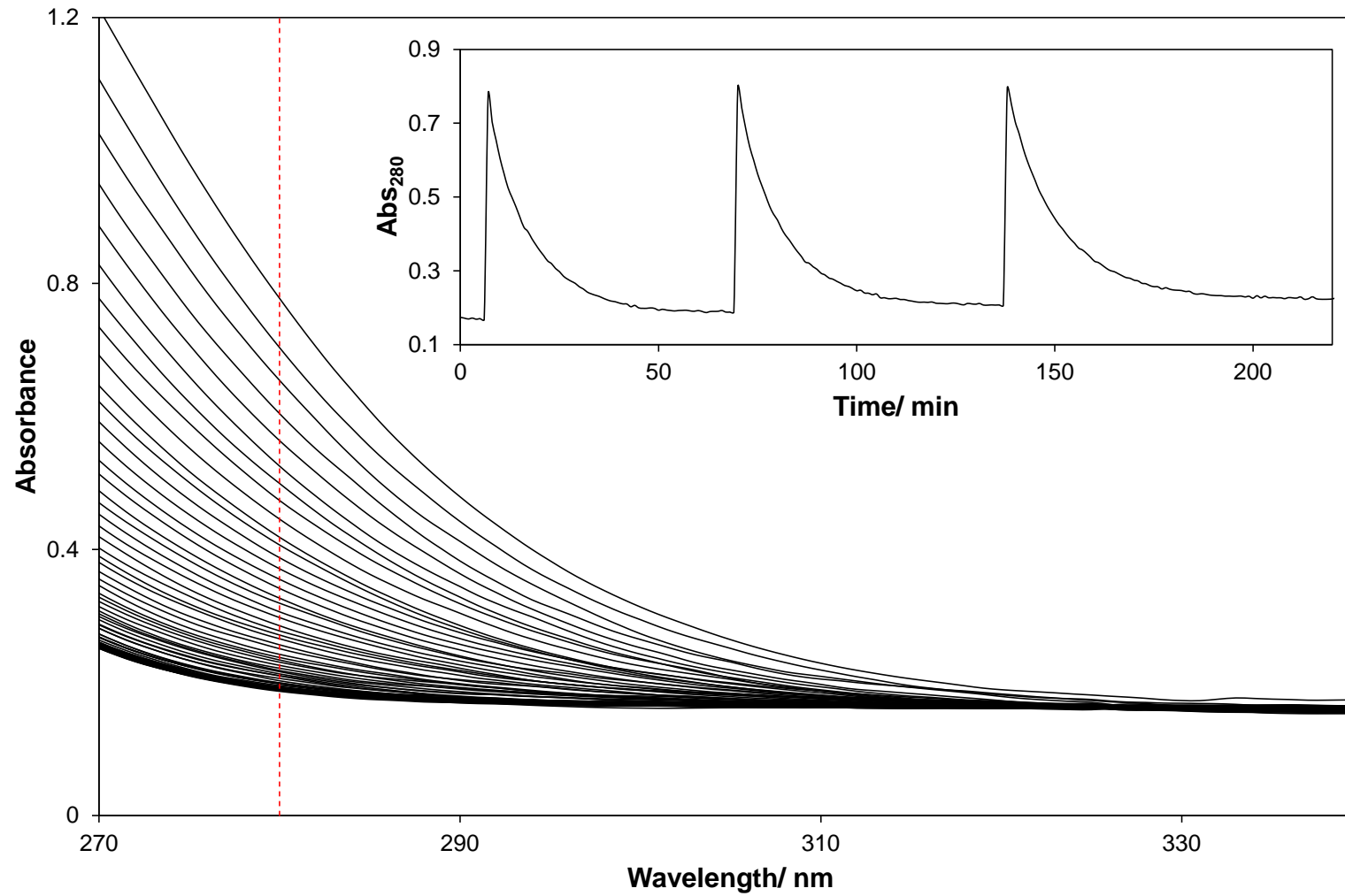


Figure 6

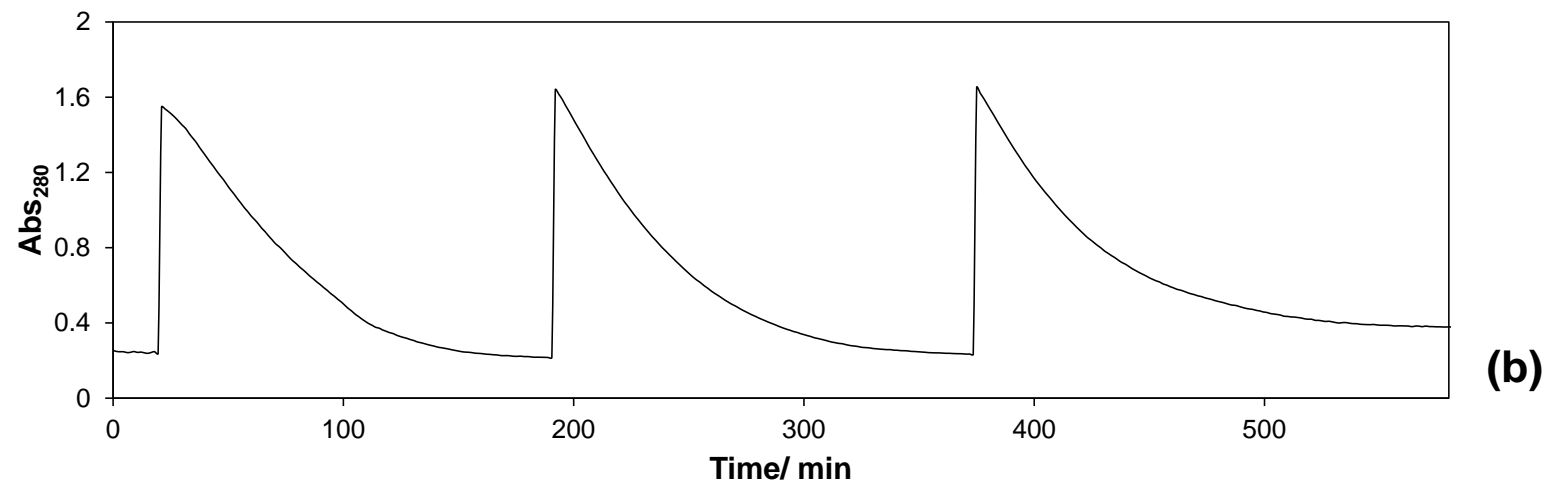
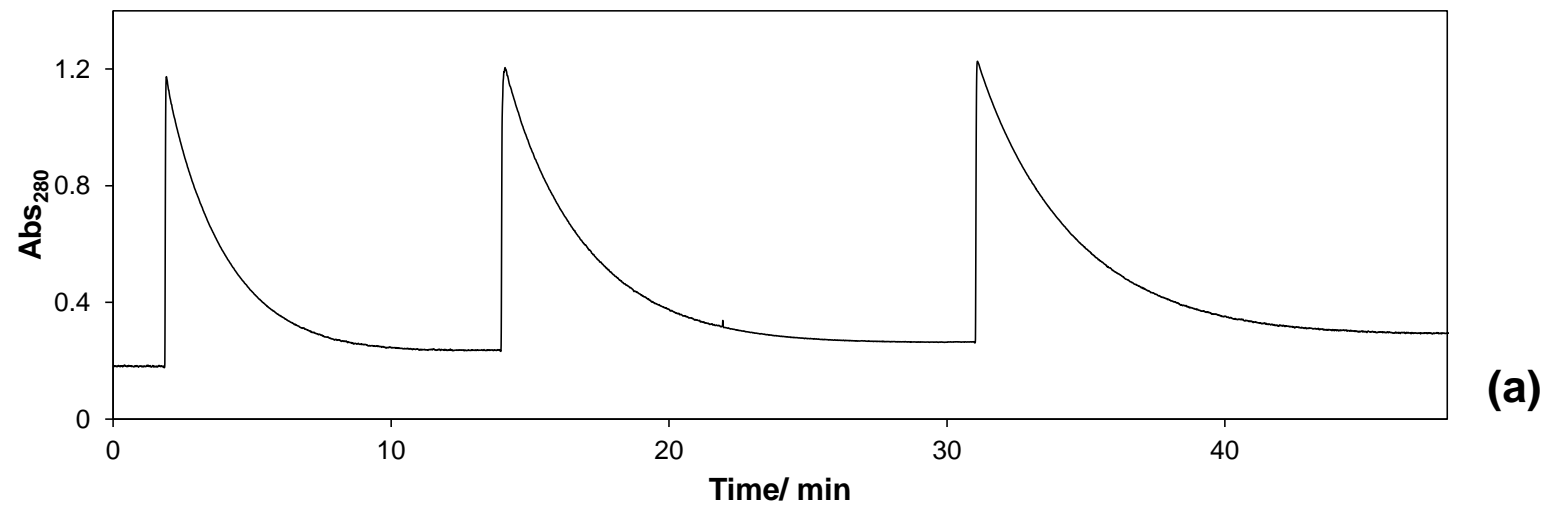


Figure 7