# Kinetic and Spectroscopic Studies with a Rapid-scanning Spectrometer. Part 2.[1] Intermediates in the One-equivalent Metal Ion Oxidation of Phenothiazine and Phenoxazine

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The one-equivalent oxidations of phenothiazine and phenoxazine (Ar_2NH) in neutral and acidic CH_3CN solution by Ce^{IV} and Fe^{III} have been analysed kinetically into the sequence

$$Ar_2NH \xrightarrow{-e^-} Ar_2NH^{\cdot+} \xrightarrow[-H^+]{-e^-} Ar_2N^+ \longrightarrow product$$
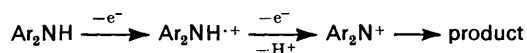
and values (or limits) for the relevant rate constants, including those for the oxidant–cation radical reaction, obtained by stopped-flow or rapid-scanning spectrometry. The latter technique has provided u.v.–visible spectra of all the intermediates involved, of which some are described for the first time.

PHENOTHIAZINE (1a) and phenoxazine (1b) are known to undergo oxidation readily in a series of one-electron steps and these stages have been described in detail for (1a).[2-9] The inter-relationships between (1a), the derived phenothiazine radical-cation (2a), the neutral phenothiazinyl radical (3a), and the diamagnetic phenothiazinium ion (4a) have been extensively studied by Hanson and Norman [9] using acetonitrile as solvent.

Analogous radicals and ions have been observed for phenoxazine [5-8] (2b)—(4b), but their electronic spectra have not been reported in detail and few kinetic data are
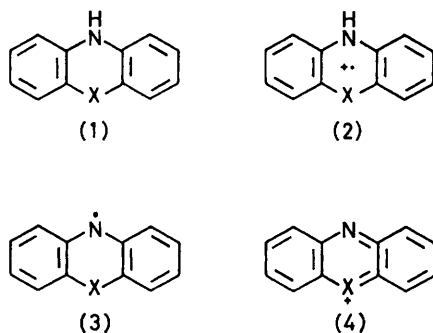

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a; X = S
b; X = O
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available. In previous oxidation studies the radicals have been generated by oxidation with concentrated sulphuric acid,[3,5] DMSO–acetic anhydride (DMSO = dimethyl sulphoxide),[6] iodine in DMSO,[6] and aluminium trichloride in nitromethane,[8] and by electrochemical oxidation [2] and flash photolysis.[7] In this study the oxidations of phenothiazine and phenoxazine have been effected by cerium(IV), bromine, and iron(III) perchlorate in acetonitrile. The two substrates were investigated by rapid-scanning spectrometry (RSS) in order to separate the successive stages of the oxidation reaction both kinetically and spectrophotometrically. In addition to placing the spectroscopy of (2b)—(4b) on a firmer basis, we hoped to add to the rather sparse information available concerning the oxidation of radical intermediates by metal-ion oxidants.

EXPERIMENTAL

RESULTS AND DISCUSSION

Cerium(IV) ammonium nitrate is fairly soluble in acetonitrile (this solution having been used as an oxidant in organic synthesis); the solution is reasonably thermally stable but slow reduction does occur which appears to be photo-catalysed.

Preliminary experiments on the oxidation of (1a) by Ce^{IV} in acetonitrile showed that a series of rapid colour changes occur. With Ce^{IV} in excess, a peak was observed at 418 nm which slowly disappeared, and with phenothiazine in excess various transient absorptions were observed with subsequent formation of a dark green solution. When stoicheiometric amounts [Ce^{IV} : (1a) = 1 : 1] were mixed, transient peaks were observed at 419 and 518 nm with subsequent appearance of the green compound ($\lambda_{max.}$ 445 and 625 nm). The dark green compound has been observed before,[9-11] but attempts to isolate it have proved unsuccessful. Hanson and Norman [9] have proposed that it is the binuclear cation (5a) which explains why it is not produced when

Ce^{IV} is in excess. The other transient species are no doubt the radical-cation (2a) ($\lambda_{max.}$ 437 and 516 nm) and the phenothiazinium ion (4a) ($\lambda_{max.}$ 419 nm). Multiplex scans showed the rapid disappearance of (2a) and the synchronous formation of (4a) when excess of Ce^{IV} is used; *cf.* Figure 1 for oxidation of (2b).

Similar experiments with phenoxazine (1b) produced analogous results. With Ce^{IV} in excess a peak at 419 nm was observed which slowly disappeared, and with (1b) in excess, various transient colour changes were observed to give finally an indigo solution ($\lambda_{max.}$ 410, 530sh, and 590 nm). When stoicheiometric amounts (*i.e.* 1 : 1) were mixed, various peaks were observed ($\lambda_{max.}$ 355, 360, 368, and 530 nm). The region 400—550 nm was studied by rapid-scanning spectrophotometry. On mixing Ce^{IV} (6.0 × 10^{-4} mol dm^{-3}) with (1b) (6.0 × 10^{-5} mol dm^{-3}) in acetonitrile the initially formed spectrum ($\lambda_{max.}$ 530 and 480sh nm) rapidly decayed with

(5)a; X = S
b; X = O
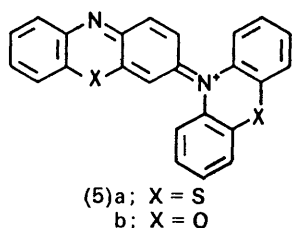
concomitant formation of a peak at 420 nm which subsequently decayed slowly; *cf.* Figure 1. It seems likely that the initial spectrum is that of (2b) ($\lambda_{max.}$ 535 nm) and such an assignment is in agreement with that of Weiss *et al.*[6] who studied the flash photolysis of (1b) in organic solvents. The subsequently formed peak at 419 nm is probably due to the phenoxazinium ion (4b) by analogy with (4a); this appears to be the first report of the electronic spectrum of this species. The indigo compound observed when (1b) is in excess could be a binuclear cationic species (5b) of the type (5a).

Phenothiazine Radical-cation (2a).—Billon[2] in his electrochemical oxidation of (1a) in an acidic medium (0.1 mol dm^{-3} $HClO_4$ in MeCN) and Hanson and Norman[9] have shown that the perchlorates of (2a) and (4a) are stable in dry acetonitrile. When the Ce^{IV} oxidation of phenothiazine was carried out in acetonitrile containing perchloric acid with the organic substrate in excess, the initially formed spectrum of (2a) was stable and decay to the green dimeric species as before did not occur. Quantitative tests were carried out to determine the extinction coefficients for this spectrum. Assuming that the formation of (2a) is stoicheiometric, the extinction coefficients were calculated by the addition of known concentrations of Ce^{IV} to a *ca.* 10-fold excess of phenothiazine in acetonitrile containing perchloric acid (20 µl of 60% AnalaR perchloric acid in 3 ml of MeCN) and recording the spectra. The averaged results (for six Ce^{IV} concentrations) were: ε_{437} 5 300 ± 200, ε_{498} 6 500 ± 200, and ε_{517} 8 700 ± 300 dm^3 mol^{-1} cm^{-1}. Since these values are *ca.* 20% higher than those of the earlier work,[9] repeat determinations were carried out

with iron(III) perchlorate as oxidant. The values obtained (ε_{437} 5 500 ± 200, ε_{498} 6 700 ± 200, and ε_{517} 8 700 ± 300 dm^3 mol^{-1} cm^{-1}) are in good agreement with the determinations using Ce^{IV}.

The discrepancy could arise for several reasons, *viz.* non-stoicheiometry or oxidation by perchlorate or dissolved oxygen. Prior nitrogen-flushing of the solutions had no effect on the spectrum. Perchloric acid was found to initiate the oxidation of (1a) to (1b), but varying the concentration of perchloric acid in the solution had no effect on the final optical densities.

Phenoxazine Radical-cation (2b).—The Ce^{IV} oxidation of (excess) (2b) in acidified acetonitrile produced the radical-cation which was stable to further oxidation. Quantitative determinations were carried out as with (1a), using Ce^{IV} as oxidant, and the results, based on measurements with six Ce^{IV} concentrations are: ε_{381} 4 100 ± 100, ε_{406} 5 200 ± 200, and ε_{529} 14 100 ± 300 dm^3 mol^{-1} cm^{-1}.

Phenothiazinium Ion (4a).—The slow decomposition of (4a) produced in the oxidation of (1a) by excess of Ce^{IV} prevented a static quantitative determination of the spectrum; investigation of the reaction by rapid-scanning techniques showed that (2a) is formed within the deadtime of the stopped-flow apparatus and is then rapidly transformed to (4a) which itself slowly disappears. There are isosbestic points in the regions 435—440 and 535—540 nm for the reaction (2a) ⟶ (4a), indicating that the oxidation is stoicheiometric. Quantitative determinations were carried out by rapid-scanning
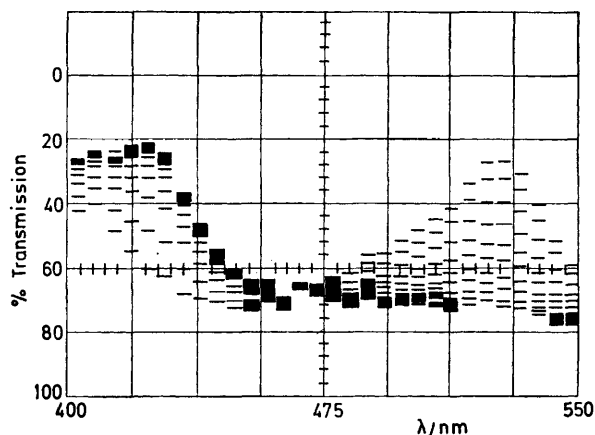
FIGURE 1 RSS trace showing the oxidation of (2b) ($\lambda_{max.}$ 520 nm) to (4b) ($\lambda_{max.}$ *ca.* 425 nm) by excess of Ce^{IV} in acidified acetonitrile. [Ce^{IV}] = 1.0 × 10^{-4} mol dm^{-3}, [(1b)] = 2.0 × 10^{-5} mol dm^{-3}, [$HClO_4$] = 40 µl (60%) in 10 cm^3 at MeCN, T = 298 K, interval between scans 20 ms

spectroscopy using excess of Ce^{IV} and various concentrations of (1a) in acidified acetonitrile. The maximum absorption at 415—420 nm was recorded and the results were corrected for Ce^{IV} absorption at this wavelength. The maximum concentration of (4a) depends on the stoicheiometry of the reaction and the ratio of the rate of formation to the rate of decay of the ion. The rate of decay of (4a) is *ca.* one-twentieth of the rate of formation, so the maximum concentration of (4a) will be *ca.* 0.85

times the concentration of (2a). Assuming the stoicheiometry is correct, this gives an estimate of ε_{419} as *ca.* 9 400 (*cf.* ε_{419} 12 600 dm³ mol⁻¹ cm⁻¹).[8]

Phenoxazinium Ion (4b).—Phenoxazine (1b) behaves in a similar manner to (1a); thus rapid-scanning trace (Figure 1) shows the simultaneous disappearance of (2b) with the appearance of a peak at 420—425 nm due to (4b). A lower limit for the extinction coefficient of (4b)

TABLE 1

Absorption peaks for radicals and ions derived from phenothiazine and phenoxazine in CH_3CN

	$\lambda_{max.}$/nm (log ε/dm³ mol⁻¹ cm⁻¹)	Ref.
Phenothiazine (1a)	254 (4.73); 320 (3.71)	9
	254 (4.66); 318 (3.68)	*a* (unspecified solvent)
	254 (4.7); 317 (3.6)	This work
Phenothiazine radical cation (2a)	271 (4.73); 437 (3.64); 516 (3.84)	9
	437 (3.7); 498 (3.8); 517 (3.9)	This work
Phenothiazinyl radical (3a)	268 (—); 344 (3.75); 381 (4.00)	9
	344 (*ca.* 3.5); 380 (*ca.* 3.9)	This work
Phenothiazinium ion (4a)	281 (4.75); 419 (4.10)	9
	419 (*ca.* 4.0)	This work
Binuclear cation (5a)	320 (4.40); 446 (4.18); 620 (4.33)	9
	445 (—); 625 (—)	This work
Phenoxazine (1b)	239 (4.66); 318 (3.93)	*a* (unspecified solvent)
	234; 238 (4.6); 315 (3.9)	This work
Phenoxazine radical cation (2b)	535 (—)	7 (in ethanol)
	381 (3.6); 406 (3.7); 529 (4.2)	This work
Phenoxazinyl radical (3b)	370 (—)	7 (in ethanol)
	336 (*ca.* 3.6); 360 (*ca.* 3.9); 368 (*ca.* 3.9)	This work
Phenoxazinium ion (4b)	420 (*ca.* 4.1)	This work
Binuclear cation (5b)	410 (—); 530 (—); 590 (—)	This work

a M. P. Olmstead, P. N. Craig, J. F. Lafferty, A. M. Pavloff, and C. L. Zirkle, *J. Org. Chem.*, 1961, **26**, 1901.

can be estimated from quantitative multiplex runs, *i.e.* ε_{420} *ca.* 13 000 dm³ mol⁻¹ cm⁻¹.

Phenothiazinyl Radical (3a).—In preliminary tests (3a) was observed in good yield when bromine was used as oxidant in acetonitrile containing a small quantity of aqueous acetate buffer (pH 4). The attempted production of (3a) with Ce^IV as oxidant was less successful, but efforts to quantify the spectrum were made. The spectrum was recorded immediately after mixing Ce^IV and phenothiazine in acetonitrile containing acetate buffer (20 μl in 2.5 ml). Lower limits can be set for the extinction coefficients if we assume a 1 : 1 stoicheiometry, *i.e.* ε_{344} >3 500, ε_{380} >8 500 (*cf.* $\varepsilon_{max.}$ 5 620 and 10 000 dm³ mol⁻¹ cm⁻¹ respectively).[9]

Phenoxazinyl Radical (3b).—When bromine was added to (1b) in acetonitrile containing acetate buffer, a spectrum was obtained with $\lambda_{max.}$ 334, 360, and 368 nm. Weiss *et al.*[7] in the flash photolysis of (1b) in ethanol assigned an absorption band observed at 365 nm to (3b).

Semi-quantitative experiments with Ce^IV gave lower limits for the extinction coefficients of ε_{334} >4 000, ε_{360} >8 500, and ε_{368} >8 500 dm³ mol⁻¹ cm⁻¹.

The absorption maxima for all the radicals and ions observed are summarised in Table 1.

Kinetic Studies.—(1a) *with excess of* Ce^IV. The formation of (2a) in the first stage of the oxidation was
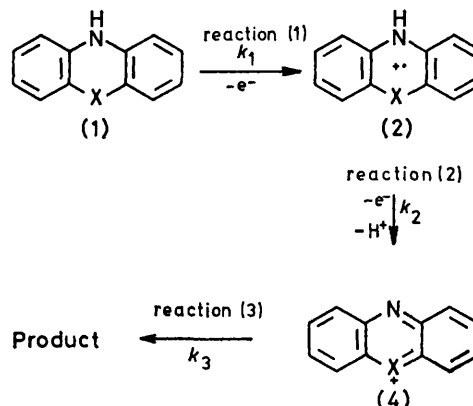
immeasurably fast, using stopped-flow methods (k_1 > 10⁶ dm³ mol⁻¹ s⁻¹). The second stage, *i.e.* the oxidation of (2a) to (4a), could be monitored by RSS, and Figure 2 shows a multiplex oscilloscope trace of this reaction at two wavelengths, *i.e.* at 525—530 nm, where (2a) is disappearing, and at 420—425 nm where (4a) is appearing. These reactions are synchronous and appeared to be first-order in substrate. At 420—425 nm there is
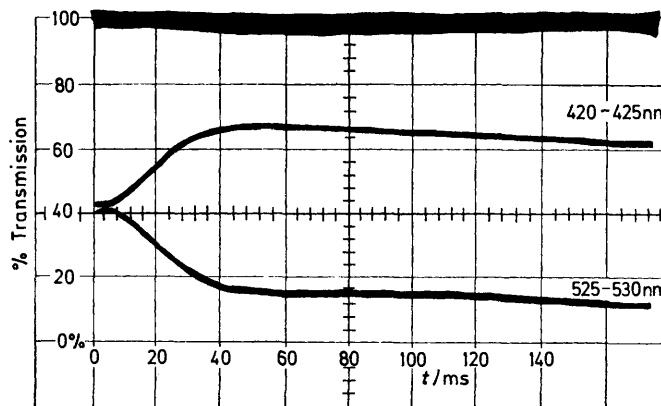
FIGURE 2 Multiplex trace showing the synchronous formation of (4a) (λ 420—425 nm) and disappearance of (2a) (λ 525—530 nm) in the Ce^IV oxidation of (1a). [Ce^IV] = 2.5 × 10⁻⁴ mol dm⁻³, [(1a)] = 2.5 × 10⁻⁵ mol dm⁻³, [HClO₄] = 40 μl (60%) in 10 cm³ of MeCN, T = 298 K

some interference from the subsequent decay of (4a) and from the decomposition in acid solution of excess of Ce^IV, which absorbs slightly at this wavelength. Both of these effects account for <10% of the absorption change in the formation of (4a). Further, single wavelength studies showed that the disappearance of (2a) at 515 nm and the formation of (4a) at 420 nm are *not* first-order, but rather zero-order in substrate and first-order in oxidant (Table 2).

(1a) *with excess of* Fe^{III}. The oxidation was also carried out with Fe^{III} perchlorate in acidified aceto-nitrile. The reaction was slower, with the weaker oxidant, but was now first-order in substrate over a

Table 2

Rate of oxidation of (2a) to (4a) using excess of Ce^{IV}

[(1a)]/ mol dm^{-3}	[Ce^{IV}] ^{a}/ mol dm^{-3}	k_0, zero order ^{b} rate constant/ mol dm^{-3} s^{-1}	k_0/ [Ce^{IV}]/s^{-1}
9.4 × 10^{-6}	1.8 × 10^{-4}	7.9 × 10^{-5}	0.44
1.9 × 10^{-5}	1.7 × 10^{-4}	7.9 × 10^{-5}	0.46
3.8 × 10^{-5}	1.5 × 10^{-4}	7.9 × 10^{-5}	0.53
1.9 × 10^{-5}	1.8 × 10^{-4}	8.3 × 10^{-5} ^{c}	0.46
2.0 × 10^{-5}	4.0 × 10^{-5}	2.4 × 10^{-5}	0.60
2.0 × 10^{-5}	1.1 × 10^{-4}	5.6 × 10^{-5}	0.51
2.0 × 10^{-5}	1.7 × 10^{-4}	6.6 × 10^{-5}	0.39
2.0 × 10^{-5}	2.3 × 10^{-4}	1.6 × 10^{-4}	0.70
2.0 × 10^{-5}	2.9 × 10^{-4}	1.9 × 10^{-4}	0.66
2.0 × 10^{-5}	3.7 × 10^{-4}	2.4 × 10^{-4}	0.65
2.0 × 10^{-5}	4.9 × 10^{-4}	3.2 × 10^{-4}	0.65

^{a} Allowing for consumption in the first oxidation stage. ^{c} 515 nm, $\varepsilon(2a)_{515} - \varepsilon(4a)_{515}$ *ca.* 7 000 dm^3 mol^{-1} cm^{-1}. ^{b} 420 nm, $\varepsilon(4a)_{420} - \varepsilon(2a)_{420}$ *ca.* 10 000 dm^3 mol^{-1} cm^{-1}. [HClO$_4$] = 40 µl of 60% HClO$_4$ in 10 cm^3 of MeCN, T = 298 K.

five-fold range of concentration, and individual runs were in agreement for 3—4 half-lives for both formation of (4a) and decay of (2a) (Table 3). The dependence on [Fe^{III}], however, seems to be somewhat greater than first-order.

Phenoxazine with excess of Ce^{IV}. In the oxidation of (1b), the formation of (2b) was again too fast to be measured ($k_1 > 10^6$ dm^3 mol^{-1} s^{-1}), but the second stage

Table 3

Rate of oxidation of (2a) to (4a) with excess of iron(III) perchlorate

[(1a)]/mol dm^{-3}	[Fe^{III}]/mol dm^{-3}	$k_{obs.}$/s^{-1} ^{a}
3.8 × 10^{-5}	2.4 × 10^{-3}	0.12
6.6 × 10^{-5}	2.4 × 10^{-3}	0.10
9.5 × 10^{-5}	2.4 × 10^{-3}	0.09
1.4 × 10^{-4}	2.4 × 10^{-3}	0.08
1.9 × 10^{-4}	2.4 × 10^{-3}	0.11
9.5 × 10^{-5}	2.4 × 10^{-3}	0.10 ^{b}
9.5 × 10^{-5}	1.0 × 10^{-3}	0.032
9.5 × 10^{-5}	2.0 × 10^{-3}	0.072
9.5 × 10^{-5}	4.1 × 10^{-3}	0.27
9.5 × 10^{-5}	6.2 × 10^{-3}	0.55
9.5 × 10^{-5}	8.1 × 10^{-3}	0.90
9.5 × 10^{-5}	1.0 × 10^{-2}	1.27

^{a} 515 nm. ^{b} 420 nm. [HClO$_4$] = 40 µl of 60% HClO$_4$ in 10 cm^3 of MeCN, T = 298 K.

could be followed by RSS and was first-order in substrate over a range of phenoxazine concentrations, and individual runs were in agreement for at least three half-lives. The decay of (2b) was monitored at 530 nm, and Table 4 shows the expected linear dependence of the first-order rate constant on Ce^{IV} concentration, yielding a value for the rate constant of reaction (2) of 4.5 × 10^4 dm^3 mol^{-1} s^{-1}.

Phenoxazine with excess of Fe^{III}. The form of the kinetics with iron(III) perchlorate as oxidant is again first-order in substrate as with Ce^{IV}, although the reaction rate is much slower (Table 5), with $k_2 = ca.$ 3.6 × 10^2 mol^{-1} dm^3 s^{-1}.

In all cases, with the notable exception of the Ce^{IV}

reaction with (2a), the oxidation of the cation-radical is essentially bimolecular, with rate constants at 298 K in the range 10^2 to 5 × 10^4 dm^3 mol^{-1} s^{-1}, *i.e.* quite near to other values reported for reaction between resonance-

Table 4

Rate of oxidation of (2b) to (4b) with excess of Ce^{IV}

[(1b)]/mol dm^{-3}	[Ce^{IV}]/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_2/mol dm^{-3} s^{-1}
4.5 × 10^{-5}	4.9 × 10^{-4}	17	3.5 × 10^4
3.6 × 10^{-5}	4.9 × 10^{-4}	23	4.7 × 10^4
2.3 × 10^{-5}	4.9 × 10^{-4}	22	4.5 × 10^4
1.4 × 10^{-5}	4.9 × 10^{-4}	20	4.1 × 10^4
4.5 × 10^{-6}	4.9 × 10^{-4}	16	3.3 × 10^4
1.3 × 10^{-5}	1.2 × 10^{-4}	5.4	4.5 × 10^4
1.3 × 10^{-5}	2.5 × 10^{-4}	12	4.8 × 10^4
1.3 × 10^{-5}	3.7 × 10^{-4}	14	3.8 × 10^4
3.0 × 10^{-5}	6.1 × 10^{-4}	20	3.3 × 10^4
3.0 × 10^{-5}	6.7 × 10^{-4}	30	4.5 × 10^4
3.0 × 10^{-5}	9.2 × 10^{-4}	34	3.7 × 10^4
3.0 × 10^{-5}	1.12 × 10^{-3}	42	3.8 × 10^4
3.0 × 10^{-5}	1.6 × 10^{-3}	80	5.0 × 10^4

[HClO$_4$] = 40 µl of 60% HClO$_4$ in 10 cm^3 of MeCN, T = 298 K, λ = 520 nm.

stabilised organic radicals and metal ion oxidants, *e.g.* for termination of growing polyacrylamide radical by aquo- and chloro-complexes of Fe^{III} and Cu^{II} [12] and for oxidation of diphenylpicrylhydrazyl and galvinoxyl by acetates of Pb^{IV}, Fe^{III}, Ce^{IV}, Co^{III}, [13] and metal halides [14] respectively. The mechanism of Ce^{IV} oxidation of (2a)
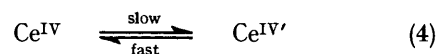
Table 5

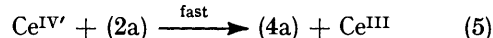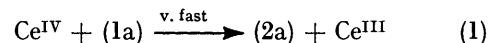The rate of oxidation of (2b) to (4b) with excess of iron(III) perchlorate

[(1b)]/mol dm^{-3}	[Fe^{III}]/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_2/mol^{-1} dm^3 s^{-1}
6.2 × 10^{-5}	1.0 × 10^{-3}	0.078	80
6.2 × 10^{-5}	2.0 × 10^{-3}	0.32	160
6.2 × 10^{-5}	4.1 × 10^{-3}	1.22	300
6.2 × 10^{-5}	6.2 × 10^{-3}	2.15	350
6.2 × 10^{-5}	8.1 × 10^{-3}	2.96	370
6.2 × 10^{-5}	1.0 × 10^{-2}	3.68	370

[HClO$_4$] = 40 µl of 60% HClO$_4$ in 10 cm^3 of MeCN, T = 298 K, λ = 525 nm.

is interesting: the kinetic rate law implies some pre-equilibrium process involving the oxidant [reactions (4), (1), and (5)], *i.e.* the measured rate refers to the con-

$$Ce^{IV} \underset{fast}{\overset{slow}{\rightleftharpoons}} Ce^{IV\prime} \qquad (4)$$

major form in   minor reactive
solution   form

$$Ce^{IV} + (1a) \xrightarrow{v.\,fast} (2a) + Ce^{III} \qquad (1)$$

$$Ce^{IV\prime} + (2a) \xrightarrow{fast} (4a) + Ce^{III} \qquad (5)$$

version (4) which is dependent only on [Ce^{IV}] and not the oxidation step (5). It is curious that the zero-order behaviour does not extend to oxidation of (2b) to (4b), which displays a large second-order rate constant.

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