Turk J Chem
27 (2003) , 695 – 702.
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Kinetics of Oxidation of Pyridylmethylsulphinylbenzimidazole by Cerium(IV) in an Aqueous Perchloric Acid Medium

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Received 09.04.2001

The kinetics of oxidation of pyridylmethylsulphinylbenzimidazole [PMSB] by Ce(IV) in an aqueous perchloric acid medium at a constant ionic strength of 1.50 mol dm^{-3} were studied spectrophotometrically. The reaction showed first order kinetics with respect to Ce(IV) concentration and an apparent less than unit order dependence in [PMSB] and a zero order in [H^{+}]. The initial addition of products has no significant effect on the rate of the reaction. A possible mechanism is proposed here. The reaction constants involved in the mechanism have been computed. There is good agreement between the observed and calculated rate constants under different experimental conditions. The activation parameters were calculated and discussed with respect to the slow step of the proposed mechanism.

Key Words: Pyridylmethylsuphinylbenzimidazole, Cerium(IV), Oxidation, Kinetics.

Introduction

Cerium(IV) has been used as an oxidising agent and an analytical reagent, especially in an acid medium[1]. However, there has been little work on the oxidation reactions of Ce(IV) in aqueous perchloric acid media[2−4]. In a sulphuric acid medium, Ce(IV) forms[5−7] several sulphate complexes, although their role has not received much attention so far. Pyridylmethylsulphinylbenzimidazole (PMSB) is 2-[[3-methyl-4-(2,2,3,3,3-trifluoropropaxy)-2-pyridyl]methylthio]benzimidazole. PMSB in the form of sulphoxide has been used in treating ulcers (gastric and duodenal), reflux oesophagitis, hyperacidity and Zollinger-Ellison syndrome. It has a greater inhibitory effect on *Helicobacter pylori* than Omeprazole.

A literature survey reveals that there are no reports on the oxidation of PMSB by any oxidant, except in one case[8] which is patented (an oxidation study only). In the continuation of the work in our laboratory[9−11] on Ce(IV) oxidation we selected PMSB as a substrate. The present study deals with the title reaction to investigate the redox chemistry of Ce(IV), to arrive at a plausible mechanism and to determine the active form of Ce(IV) in an aqueous acidic medium.

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Experimental

Materials A stock solution of PMSB (Cipla Pharmaceuticals) was prepared by dissolving PMSB in 0.20 mol dm^{-3} sulphuric acid and ceric ammonium sulphate (s.d. fine chemicals) in doubly distilled water in the presence of 0.50 mol dm^{-3} sulphuric acid. The stock solution of Ce(IV) was standardised by known methods[12]. A Ce (III) solution was prepared by dissolving Ce(III) acetate (BDH) in water, and the concentration of Ce(III) was ascertained by standard procedures. All other reagents were of analytical grade and their solutions were prepared by dissolving the necessary amounts of the samples in doubly distilled conductivity water. $HClO_4$ and $NaClO_4$ were used to provide required acidity and to maintain ionic strength, respectively.

Kinetic measurements

All kinetic measurements were performed under pseudo first order conditions with PMSB in at least 10-fold excess over Ce(IV) at a constant ionic strength of 1.5 mol dm^{-3}. The reaction was initiated by mixing previously thermostated solutions of Ce(IV) and PMSB, which also contained the necessary quantities of $HClO_4$ and $NaClO_4$, to maintain the required acidity and ionic strength, respectively. The temperature was maintained at 26 ± 0.1 °C. The course of reaction was followed by monitoring the decrease in the absorbance of Ce(IV) in a 1 cm quartz cell of a Hitachi model 150-20 spectrophotometer at its absorption maximum of 360 nm as a function of time. Earlier, it had been verified that there is negligible interference from the other reagents at this wavelength. The application of Beer's law to Ce(IV) at 360 nm had earlier been verified, giving $\varepsilon = 3100 \pm 150$ $dm^3 mol^{-1}$ cm^{-1}. The first order rate constants, k_{obs}, were evaluated by plots of log [Ce(IV)] versus time. The first order plots in almost all cases were linear up to 75% of completion of the reaction (Figure 1), and the k_{obs} values were reproducible to within ± 5%.

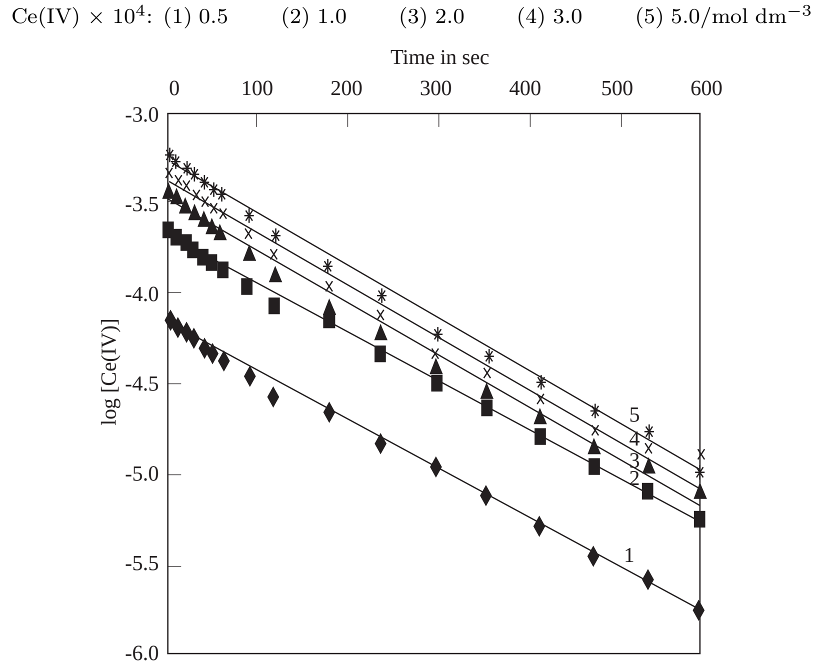
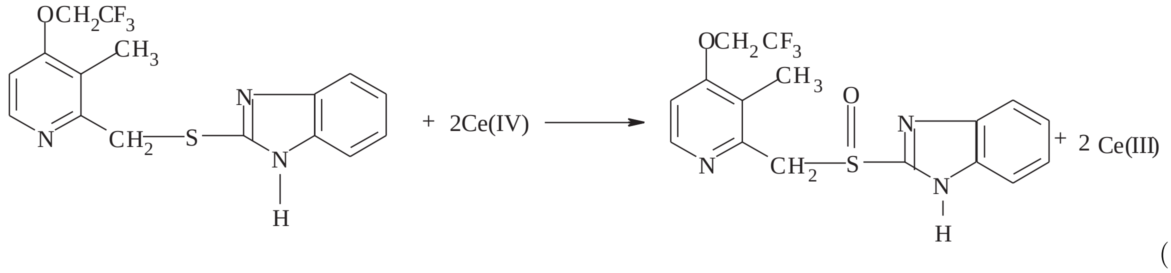


Figure 1. First order plots of on the oxidation of PMSB by Ce(IV) in aqueous acidic medium at 26°C.

Stoichiometry and reaction products

The reaction mixture containing the excess Ce(IV) concentration over PMSB was mixed in the presence of 0.15 mol dm^{-3} HClO$_4$ adjusted to a constant ionic strength of 1.5 mol dm^{-3} and allowed to react for about 8 h at 26 ± 1.0 °C. The remaining Ce(IV) was then analysed spectrophotometrically. The results indicated that 2 mol of Ce(IV) were consumed by 1 mol of PMSB, (i.e. 2:1) according to Equation 1.



(1)

The reaction products were extracted with solvent ether, and the product was subjected to TLC analysis which revealed (R$_f$ = 0.48) the presence of sulphoxide of PMSB comparing with the pure authentic sample obtained from Cipla Pharmaceuticals. The sulphoxide was also confirmed by its IR spectrum, which showed the band at 1052 cm^{-1} .

Results

Reaction order

The reaction orders were determined from the slopes of log k_{obs} versus log (concentration) plots by varying the concentration of reductant and acid in turn, while keeping the others constant. The Ce(IV) concentration was varied in the range of 5.0 x 10^{-5} to 5.0 x 10^{-4} mol dm^{-3} and the linearity of plots of log [Ce(IV)] versus time indicated a reaction order in [Ce(IV)] as unity. This was also confirmed by varying the [Ce(IV)], which did not show any change in pseudo first order rate constant k_{obs} (Table 1). The substrate, [PMSB], was varied in the range of 5.0 × 10^{-4} to 5.0 × 10^{-3} mol dm^{-3} at 26 °C keeping all other reactant concentrations and conditions constant. The apparent reaction order in [PMSB] was found to be less than unity (Table 1).

Table 1. Effect of [PMSB] and [Ce(IV)] on the oxidation of PMSB by Ce(IV) in an aqueous acidic medium at 26 °C ([H$^+$] = 0.15, I = 1.50 mol dm^{-3}).

[PMSB] × 10^3 mol dm^{-3}	[Ce(IV)] × 10^4 mol dm^{-3}	k_{obs} × 10^3(s^{-1}) Exptl*.	Calc.*
0.5	2.0	1.54	1.55
1.0	2.0	2.20	2.16
2.0	2.0	2.60	2.69
3.5	2.0	3.04	3.02
5.0	2.0	3.17	3.16
2.0	0.5	2.65	2.69
2.0	1.0	2.67	2.69
2.0	2.0	2.64	2.69
2.0	3.0	2.73	2.69
2.0	5.0	2.72	2.69

*Experimental and calculated

Effect of initially added products

The effect of initially added products such as Ce(III) and sulphoxide of PMSB in the concentration range of 1.0×10^{-5}- 2.0×10^{-4} mol dm^{-3} keeping all other conditions constant did not show any significant effect on the rate of reaction.

Effect of varying acidity

The effect of acid on the reaction was studied by using perchloric acid at constant concentrations of PMSB and Ce(IV) and keeping a constant ionic strength of 1.5 mol dm^{-3} at 26 °C. A constant amount of sulphuric acid from the stock solution of Ce(IV) is also present in all cases. The rate constants did not change appreciably with the increase in acid. The in situ [H$^+$] concentration in the sulphuric acid-sulphate media was calculated using the known ionisation constant[13] of acid sulphate, as in an earlier study[14]. The order in [H$^+$] was zero. Ce(IV) is known[3] to form several complexes in acid sulphate media, such as $Ce(OH)^{3+}$, $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2(HSO_4)^-$ and $H_3Ce(SO_4)_4^-$.

Effect of ionic strength and solvent polarity

The effect of ionic strength was studied by varying the sodium perchlorate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.35 to 1.5 mol dm^{-3} at constant concentrations of Ce(IV), PMSB and perchloric acid. It was determined that the rate of the reaction is independent of the ionic strength of the medium.

The relative permittivity (D) effect was studied by varying the acetic acid-water content in the reaction mixture with all other conditions being kept constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids[15]. No reaction of the solvent with the oxidant occurred under the experimental conditions used. The rate constant, k_{obs}, increased negligibly with a decrease in the dielectric constant of the medium.

Polymerisation study

The reaction mixture containing acrylonitrile was kept for 4 hours in an inert atmosphere. On diluting the reaction mixture with methanol, we obtained precipitate, indicating the presence of free radical intervention in the reaction.

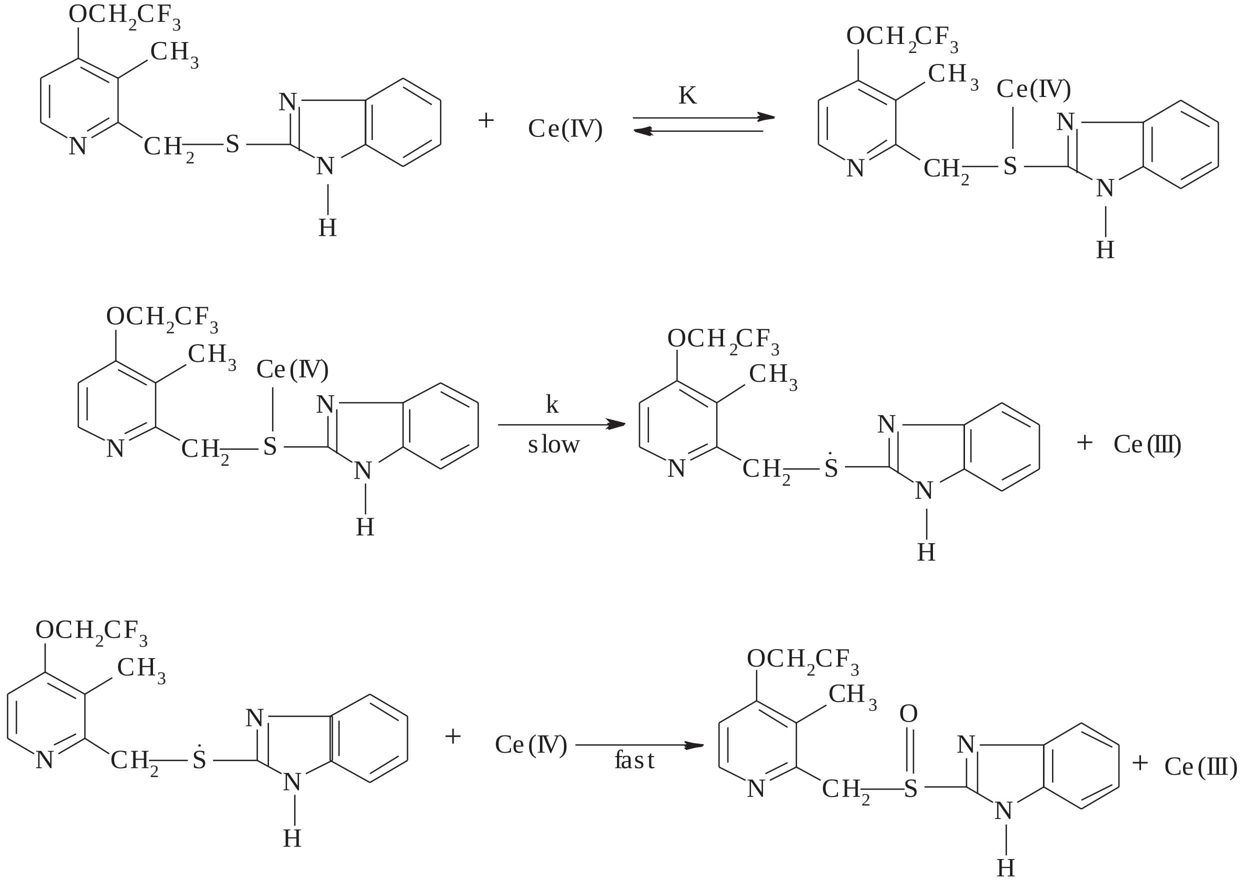
Effect of temperature

The rate constants, k, of the slow step of Scheme 1 were obtained from the intercept of the plots of $1/k_{obs}$ versus 1/[PMSB] at different temperatures and were used to calculate the activation parameters. The activation parameters corresponding to these constants were evaluated from the plots of log k vs. $1/T$ and are given in Table 2.

Discussion

The reaction between PMSB and Ce(IV) in an acidic medium has a stoichiometry of 2:1 with zero order dependence on acid and less than unit order dependence on PMSB and a first order dependence on [Ce(IV)].

No effect of the products was observed. The lack of an acid effect indicates that the usual active species of Ce(IV) in this medium, $[Ce(OH)]^{3+}$, is minimally effective, and the comparatively large unhydrolysed Ce(IV) ion is only active in Scheme 1. This type of species is also observed in earlier work[6]. The results indicate that first Ce(IV) reacts with PMSB to give a complex, which then decomposes in a slow step to give a free radical derived from PMSB and Ce(III). This free radical reacts with another molecule of Ce(IV) species in further fast step to yield the products shown in Scheme 1.



Scheme 1

Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in a sequence of one electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work[17] on the acidic Ce(IV) oxidations of various organic substrates. Spectroscopic evidence for the complex formation was obtained from the UV-vis spectra of the substrate and a mixture of substrate and oxidant. A bathochromic shift of about 4 nm, from 246 to 250 nm of Ce(IV) and hyperchromicity was observed. Analogous effects upon complex formation between the substrate and oxidant have been observed in other investigations[18−20]. The formation of complex is also proved kinetically by the non–zero intercept of the plot of $1/k_{obs}$versus 1/[PMSB] (Michaelis Menten plot).

Scheme 1 leads to the rate law given in Equation 2

$$\text{Rate} = -\frac{d[Ce(IV)}{dt} = \frac{k\ K[Ce(IV)]\ [PMSB]}{1+K[PMSB]} \tag{2}$$

Table 2. Thermodynamic activation parameters for the oxidation of PMSB by acidic Ce(IV) in an aqueous pechloric acid medium.

[Ce(IV)] = 2.0×10^{-4}, [$HClO_4$] = 0.15, I = 1.50 mol dm^{-3}

(a) Effect of temperature on the rate constant of slow step of Scheme 1.

Temp. in °C	$10^3\times$ k s^{-1}
26	3.58
31	4.79
36	5.88

(b) Activation parameters with respect to the slow step of Scheme 1.

Activation Parameters	Values
Ea (kJ mol^{-1})	40 ± 2
Δ $H^{\#}$(kJ mol^{-1})	37 ± 2
Δ $S^{\#}$(J $K^{-1}mol^{-1}$)	-168 ± 4
Δ $G^{\#}$(kJ mol^{-1})	88 ±3

In fact the Equation 2 should also contain the term K [Ce(IV)] + K^2 [Ce(IV)] [PMSB] in the denominator on right hand side, which is neglected in view of the low concentration of [Ce(IV)]. Equation 2 can be written as Equation 3

$$\frac{\text{Rate}}{[Ce(IV)]} = k_{\text{obs}} = \frac{k\ K\ [PMSB]}{1 + K[PMSB]} \tag{3}$$

Equation 3 can be rearranged to give Equation 4 which is suitable for verification.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK\ [PMBS]} + \frac{1}{\mathbf{k}} \tag{4}$$

According to Equation 4, plots of 1/k_{obs} versus 1/[PMSB] should be linear. This is verified in Figure 2. From the slope and intercept of such a plot the calculated values of K and k were 1.53 ± 0.07 × 10^3 dm^3 mol^{-1}, 3.58 ± 0.17 × 10^{-3} s^{-1}, respectively. Using these values in Equation 3, rate constants were calculated over a range of different conditions and compared with the experimental values as given in Table 1. There is reasonable agreement between the calculated and experimental rate constants, supporting the assumptions in Scheme 1.

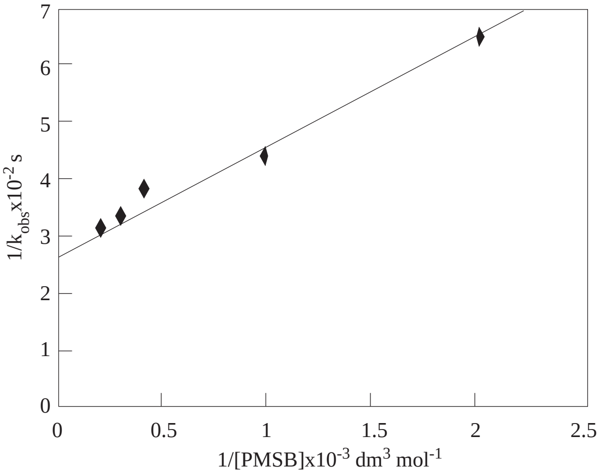


Figure 2. Verification of rate law Equation 3 (Conditions as in Table 1.)

The negligible effect of ionic strength and relative permittivity on the rate of reaction qualitatively explains the reaction between a positive and neutral species as shown in Scheme 1. The effect of solvent on the rate of reaction has been discussed in the literature[21−23].

The high negative value of $\Delta S^{\#}$ indicates the formation of complex in the reaction, and the complex is more ordered than the reactants[24−25]. The observed modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner-sphere mechanism[26−29].

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