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ORIGINAL ARTICLE

Micellar effect on the kinetics of oxidation of methyl blue by Ce(IV) in sulfuric acid medium

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Abstract The kinetics of oxidation of methyl blue (MB) by Ce(IV) in aqueous and surfactant media has been carried out to explore the micellar effect on the rate and kinetic parameters of the reaction. The reaction was found to be first order with respect to both oxidant and substrate and fractional order with respect to H^+. The active kinetic species of the oxidant was found to be $Ce(SO_4)^{+2}$ based on the effect of ionic strength and sulfate ion on the rate of the reaction. The presence of micelles was found to inhibit the reaction and this effect has been explained by the association of one of the reactants with the micelles leaving the other reactant in the bulk solution. The binding constant and first order rate constant in micellar medium has been obtained by the application of pseudo-phase model to the experimental data. Interestingly, the temperature dependence of the reaction reveals that the reaction has negative activation energy in the absence of micelles, which turns to a positive value in the presence of micelles.

1. Introduction

Methyl blue (Scheme 1) belongs to the group of triaminotriphenylmethane dyes. Methyl blue, aniline blue, and water blue are usually mixtures of the same components. Methyl blue and aniline blue are so similar that both dyes are recorded under the color index name “Acid blue 93”. They are widely used as antiseptic dyes in polychrome staining methods and have applications in histological and microbiological staining solutions (Kotak et al., 1997; Yücesoy et al., 2001). Methyl blue has been used as a model to study the effect of various catalysts on photodegradation of dyes (Yu et al., 2004; Kumar et al., 2010).

The presence of surfactants along with the dye solution was found to impose some association between the dye and the surfactants and this was found to affect some properties of the dye, such as improve solubility, accelerate adsorption on fibers and strengthen dye binding (Guo et al., 1994; Simoncic and Kert, 2002). The presence of surfactants in the reaction media was found to have either catalytic or inhibition effect (Zaheer

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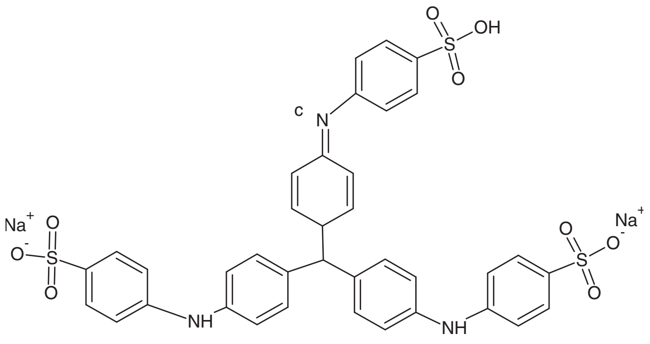


Scheme 1

and Rafiuddin, 2009; Akram et al., 2010). These materials aggregate in the aqueous solution to form colloidal structures called micelles that act as sites for the reaction (Mallick et al., 2001).

This work is an attempt to study the effect of the presence of surfactants in the reaction of the dye with oxidants. Chemical oxidation of methyl blue by Ce(IV) in the presence of the nonionic surfactant TritonX-100 (TX-100) has been selected as the model reaction. The results were interpreted by means of a pseudo-first order theoretical model. In addition, the reaction has been carried out in the absence of the surfactant for comparison.

2. Experimental

2.1. Materials

Cerium sulfate and sulfuric acid were of AR grade purity and purchased from Fisher Scientific, UK. Methyl blue, (MB) sodium sulfate, and sodium chloride were also of AR grade, purchased from Avondale Laboratories, UK. TX-100 and Sudan-III, GR grade, were from Avonchem UK. Stock solutions of cerium sulfate (0.05 mol dm^{-3}) in 0.5 mol dm^{-3} sulfuric acid and methyl blue (2.5×10^{-4} mol dm^{-3}) in water were prepared and covered with aluminium foil. Doubly distilled water was used throughout all preparations and experiments.

2.2. Kinetic measurements

The required volumes of methyl blue and sulfuric acid were transferred to the reaction vessel, which is thermostated along with the required volume of cerium sulfate solution to the desired temperature. The concentration of Ce(IV) was kept in large excess over the concentration of MB to achieve the pseudo-first order conditions. After thermal equilibrium, the two solutions were mixed throughly and the absorbance of the mixture was followed at subsequent time intervals at $\lambda_{\max}$ of methyl blue (600 nm) using a Unico UV-2100 Spectrometer. The rate constants were evaluated from the linear plots of log(Absorbance) against time. To obtain the activation parameters, the temperature of the reaction has been varied over the range 283–316 K.

2.3. Stoichiometry and product analysis

Stoichiometry of the reaction was estimated by preparing several solutions of MB and Ce(IV), in which the concentration of MB was in excess over that of Ce(IV). The absorbance of these mixtures was measured after 24 h. The calculations stated that 6 mol of Ce(IV) are consumed by each mole of MB. The UV–vis spectra of methyl blue, cerium sulfate and the product of the reaction are shown in Fig. 1. The product of the reaction was found to be of violet color and has a broad peak with $\lambda_{\max}$ at about 480 nm. This color was stable for long time after the reaction is over, which indicated that it is the final product at these reaction conditions. This can be explained by the fact that the center of the reaction occurs at auxochrome which is indicated by the letter "c" in Scheme 1. From these observations, the stoichiometry of the reaction may be represented as in the following equation:

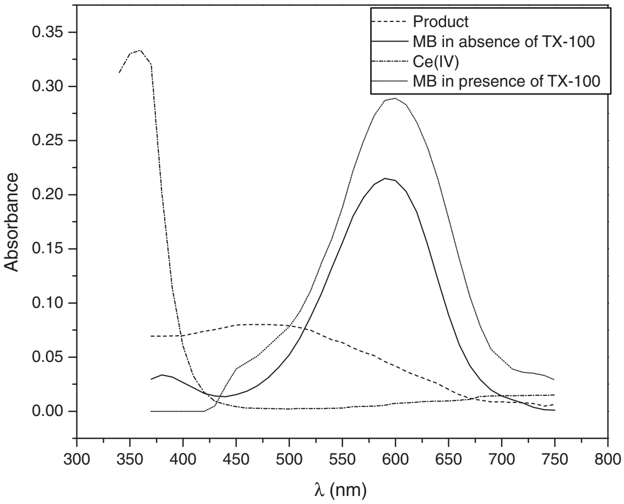


Figure 1 UV–vis spectra of methyl blue in the absence/presence of TX-100, Ce(IV) in 0.5 mol dm^{-3} H_2SO_4 and product of the reaction.

$$\mathrm{C_{37}H_{27}N_3S_3O_9 \cdot 2Na + 6Ce^{+4} + 3H_2O \rightarrow C_{30}H_{22}N_3S_2O_6CO \cdot 2Na + C_6H_5SO_3NO_2 + 6Ce^{+3} + 6H^+} \quad (1)$$

3. Results and discussion

3.1. Reaction time curves

The plots of lnA against time, at various temperatures and Ce(IV) concentration and fixed MB concentration in the absence/presence of TX-100, are shown in Fig. 2. All the plots are linear indicating that the reaction is first order with respect to MB. The observed rate constants for the reaction have been calculated from the slopes of the plots using the linear regression method.

3.2. Effect of MB concentration

Slight increase in k_{obs} value has been observed with decreasing the concentration of MB. This can be explained by the fact that MB occurs in the solution in the form of two species in equilibrium according to the following equation:

$$\mathrm{MB + H_2O \rightleftharpoons MBH + OH^-} \quad (2)$$

Now according to the abovementioned equation, dilution of the solution (decreasing the concentration of MB) will direct

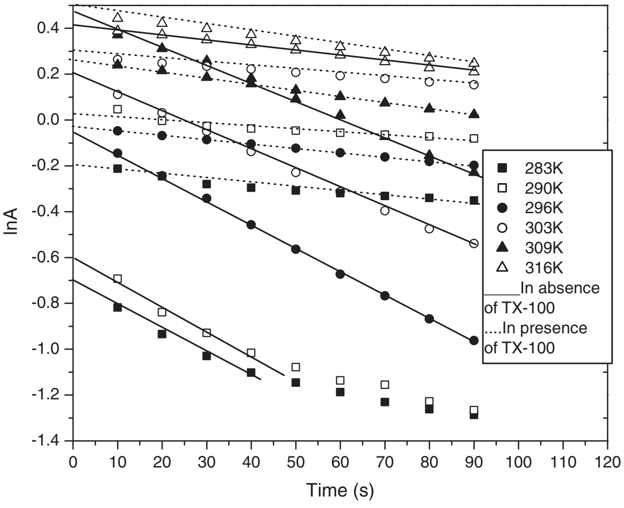


Figure 2 Pseudo first-order plots in the absence and presence of TX-100 and at following conditions: $[MB] = 5\times10^{-5}$ moldm^{-3}, $[Ce(IV)] = 4.0\times10^{-4}$ moldm^{-3} and $[H_2SO_4] = 4\times10^{-3}$ moldm^{-3}.

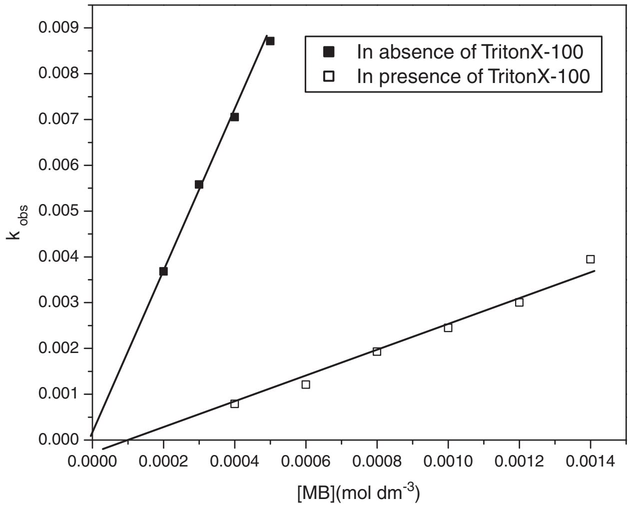


Figure 3 k_{obs} vs. concentration of Ce(IV) in the absence/presence of TX-100 at the following conditions: $[MB] = 5\times10^{-5}$ moldm^{-3}, $[H_2SO_4] = 4\times10^{-3}$ moldm^{-3} and $[TX\text{-}100] = 0.0093$ moldm^{-3} and at 297 K.

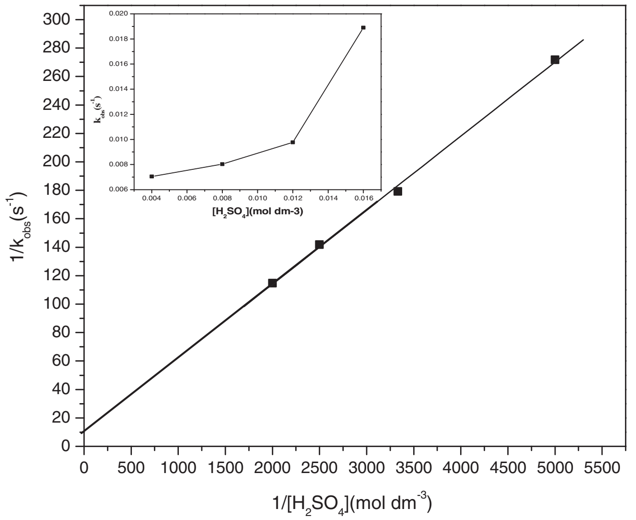


Figure 4 $1/k_{obs}$ vs. $1/[H_2SO_4]$ at the following conditions: $[MB] = 5\times10^{-5}$ moldm^{-3}, $[Ce(IV)] = 4.0\times10^{-4}$ moldm^{-3} and at 297 K. The inset shows k_{obs} vs. $[H_2SO_4]$.

the reaction toward the formation of MBH, which appears to be a more reactive species. Meenakshisundaram and Vinothini have obtained similar results with the oxidation of substrate by Cr(VI) and they have given similar explanation (Meenakshisundaram and Vinothini, 2003).

3.3. Effect of Ce(IV) concentration

It was found that k_{obs} increases linearly with increasing concentration of Ce(IV) in both the presence/absence of TX-100. Fig. 3 shows the plots of these results, where we can see that the data have been fitted into straight lines successfully ($r > 0.994$) with intercepts close to zero. This indicates that the reaction is first order with respect to Ce(IV). The second order rate constants (k_2) at 297 K in the absence/presence of TX-100 have been calculated from the slopes of the plots in Fig. 3 and found to be 16.54 and 3.09 mol^{-1} dm^3 s^{-1}, respectively. These values show clearly the inhibition effect of TX-100.

3.4. Effect of sulfuric acid solution

The values of k_{obs} at different concentration of sulfuric acid have been plotted and shown in the inset of Fig. 4. The plot is not linear but the plot of $1/k_{obs}$ versus 1/[sulfuric acid] (Fig. 4) gave straight line with positive intercept on the y axis. If we assume that $[HSO_4^-] = [H^+]$, then the reaction is of fractional order with respect to $[H^+]$.

3.5. Effect of ionic strength

The k_{obs} value was found to be diminished with the addition of sodium chloride solution. Fig. 5 shows the plot of log k_{obs} against the square root of ionic strength of the solution. As expected the plot is linear with a slope (z_Az_B) of -3.22 and an intercept at -1.99. The negative value of the slope dictates that the reactants in the rate-determining step are of opposite charges, and its magnitude cannot be attributed to the dipolar reactants. Hence the reactants should carry pronounced charges (Laidler, 1987). Since MB has a pronounced charge of -2, then Ce(IV) should be in the form that is about double positively charged. It was reported that Ce(IV) exists in aqueous sulfuric acid in several forms, such as Ce^{+4}, $CeSO_4^{+2}$, $Ce(SO_4)_2$, $Ce(SO_4)_3$, $HCe(SO_4)_3^-$, $HCe(SO_4)_4^{-3}$, $H_2Ce(SO_4)_4^{-2}$, $H_3Ce(SO_4)_4^-$ and $H_4Ce(SO_4)_4$ and the reactive species depends on the substrate (Bilehal et al., 2003; Adari et al., 2008; Grover et al., 1970; Grover and Gupta, 1969). Our results suggest that the reactive species in this work is $CeSO_4^{+2}$ which is in agreement with the results reported by Moore and Anderson (Moore and Anderson, 1944). To confirm this finding, several kinetic runs were performed in the presence of sodium sulfate in the reaction mixture with keeping all other conditions fixed (Sumathi et al., 2010). Slightly diminished values of k_{obs} were obtained due to the conversion of positively charged species

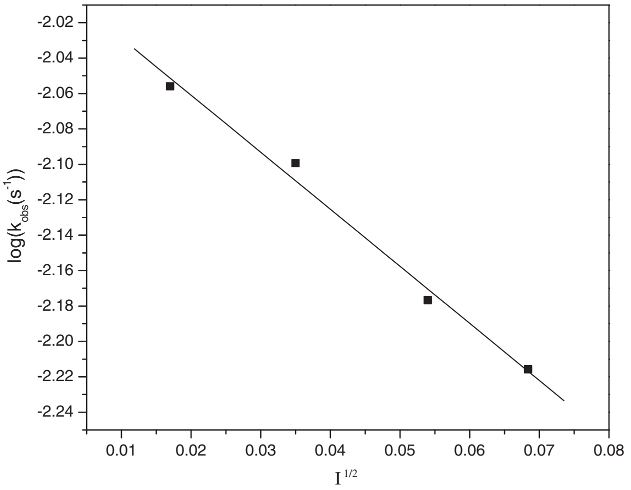


Figure 5 log k_{obs} vs $I^{1/2}$ at various concentrations of KCl at following conditions: [Ce(IV)] = 4.0×10^{-4} moldm^{-3} [MB] = 5×10^{-5} moldm^{-3}, [H_2SO_4] = 4×10^{-3} moldm^{-3} and 297 K.

$CeSO_4^{+2}$ to other neutral or negatively charged ones. The k_{obs} at infinite dilution at these experimental conditions was calculated from the intercept and found to be 0.01 s^{-1}.

3.6. Micellar effect

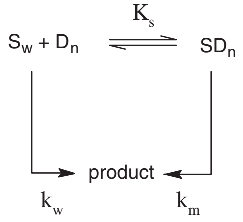
Th presence of TX-100 in concentrations above those of CMC in the reaction mixture caused the k_{obs} value to decrease significantly. The k_{obs} values have been plotted against the concentration of TX-100 in Fig. 6, where we can see that k_{obs} diminishes quickly with increasing the concentration of the surfactant till the concentration reaches the value of about 0.01 mol dm^{-3} after which the rate constant becomes almost constant. Several models have been postulated to interpret the effect of the concentration of surfactant on the rate of the reactions. Pseudo-phase model suggested by Mengo and Bortany assumes that the substrate is distributed between water and micellar phases; hence, the overall rate will be the sum of the rates in water and in the micelles (Scheme 2).

Catalytic effect occurs when both reactants bind to the micelle and react to give the product. However, when one of the reactants binds to the micelle while the other remains in the bulk solution, the reaction gets inhibited. The model leads to the following equation:

$$\frac{1}{k_{obs} - k_w} = \frac{1}{k_m - k_w} + \frac{1}{(k_m - k_w)K_s[D_n]} \qquad (3)$$

where k_w and k_{obs} are the observed rate constants in the absence and in the presence of TX-100, respectively, k_m is the micellar rate constant, K_S is the binding constant and D_n = [D] CMC, [D] is the concentration of surfactant. The CMC of TX-100 has been examined experimentally by dye solubilization method using Sudan-III (Duff and Gilf, 1972), and found to be 33.0×10^{-5} mol dm^{-3}. The previous equation allows the calculation of k_m and K_s by plotting $\frac{1}{k_w - k_{obs}}$ versus $\frac{1}{[D_n]}$. This plot is shown in Fig. 7, which is found to be a straight line as expected from the model. The values of k_m and K_s were calculated from the slope and the intercept of the plot, and found to be 7.70×10^{-4} s^{-1} and 203.64 mol^{-1} dm^3, respectively. The value of k_m is smaller than k_w (3.00×10^{-3} s^{-1}), which shows the micellar inhibition effect (Das, 2004).

The spectrum of MB in the presence of TX-100 (Fig. 1) shows a slight red shift of λ_{max} and an increase of the absorbance compared to that of MB in the absence of TX-100,



Scheme 2

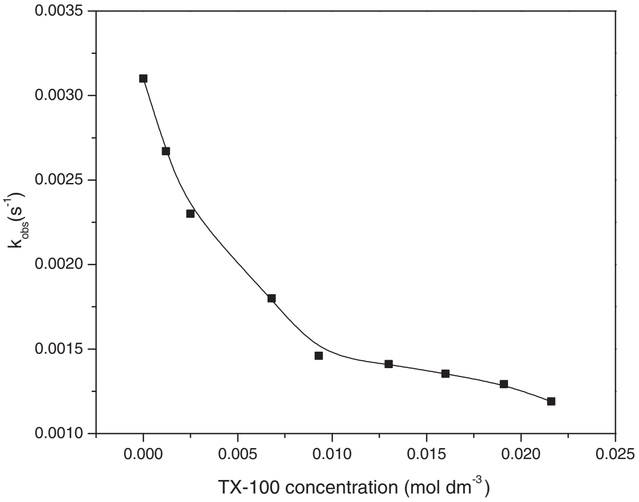


Figure 6 Variation of k_{obs} with the concentration of TX-100 at following conditions: [Ce(IV)] = 4.0×10^{-4} moldm^{-3} [MB] = 5×10^{-5} moldm^{-3}, [H_2SO_4] = 4×10^{-3} moldm^{-3} and 297 K.

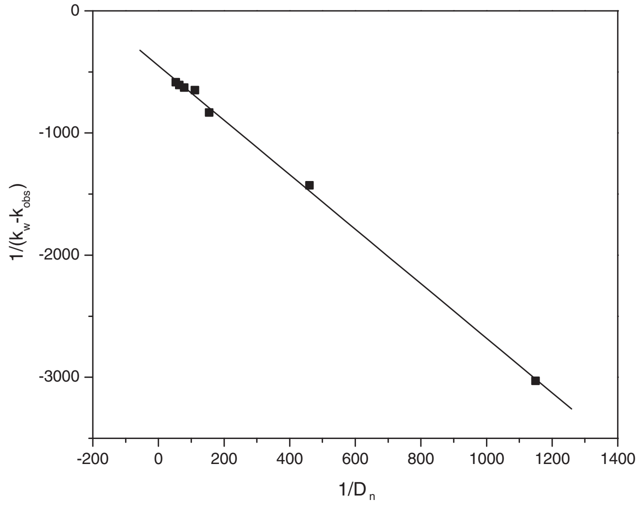


Figure 7 Pseudo-phase model plot at following conditions: [Ce(IV)] = 4.0×10^{-4} moldm^{-3}, [MB] = 5×10^{-5} moldm^{-3}, [H_2SO_4] = 4×10^{-3} moldm^{-3} and 297 K.

the phenomenon which has been interpreted is due to the association of substrate with the micelles (Sicilia et al., 1994). Therefore, the inhibition effect of TX-100, which was observed in this reaction, can be explained by the fact that the methyl blue binds itself to TX-100 leaving Ce(IV) in the bulk solution resulting in reducing the chance by which the two reactants can meet.

3.7. Temperature effect

The temperature dependence of the pseudo-first order rate constant is the most interesting aspect in this work which is its decrease with the temperature. This can be observed in Fig. 8 where lnk_{obs} has been plotted against $1/T$ both in the absence and in the presence of TX-100. The linearity of the two plots indicates that Arrhenius equation has been followed. The activation energies of the reaction in the absence/presence of TX-100 have been calculated from the slopes of the straight lines and given in Table 1. The activation energy in the absence of TX-100 is negative, which indicates that there must be at least one mechanistic step that possesses equilibrium constant, which decreases with raising the temperature. The negative activation energy can also be considered as an evidence for the involvement of free radicals in the mechanism of the reaction (Pilling, 1992). However, the presence of the surfactant in the reaction mixture increases the activation energy to a positive value to give another evidence for the inhibition effect of the micelles. Other activation parameters, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$, at 297 K have also been calculated and given in Table 1. The values of the activation entropy are high and negative indicating that the structure of the activated complex is more ordered than the structure of the reactants (Patwari et al., 2000). The values of free energy of activation both in the absence and in the presence of TX-100 are comparable which suggests that similar mechanism is operated in the two cases (Patil et al., 2007).

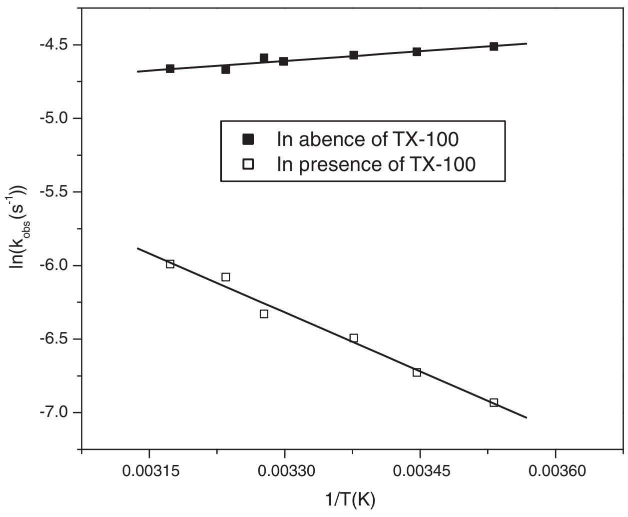
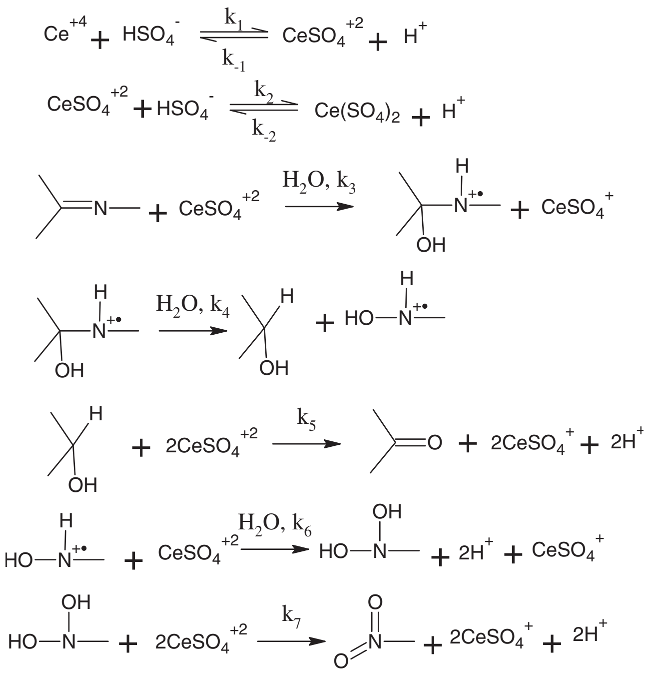


Figure 8 Plot of ln k_{obs} vs. $1/T$ in the absence/presence of TX-100 at following conditions: [Ce(IV)] = 4.0×10^{-4} moldm^{-3}, [MB] = 5×10^{-5} moldm^{-3}, [H_2SO_4] = 4×10^{-3} moldm^{-3} and [TX-100] = 0.0093 mol dm^{-3}.

Table 1 Kinetic parameters of the reaction in the absence and in the presence of TX-100 at 297.

	Ea/kJ mol^{-1}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/JK^{-1} mol^{-1}	$\Delta G^{\#}$/kJ mol^{-1}
In the absence of TX-100	−3.660	−6.129	−295.282	93.828
In the presence of TX-100	22.211	19.742	−223.674	86.173



Scheme 3

4. Mechanism

The probable mechanism of the reaction is depicted in Scheme 3, where the attack of the oxidant occurs at the imine group leading to the formation of a series of free radicals. The stable products of the reaction are the nitro and keto derivatives.

Depending on this mechanism, the rate of the reaction can be given as in the following equation:

$$-\frac{d[Ce^{+4}]}{dt} = 4k_1K\frac{[MB][Ce^{+4}][HSO_4^-]}{\frac{k_2}{k_{-1}}[HSO_4^-]+[H^+]} \qquad (4)$$

where $K = k_1/k_{-1}$, is the equilibrium constant of the first step. This equation quite agreed with the experimental findings.

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