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Kinetic and Mechanistic Aspects of Oxidation of Aminotriazole Formamidine by Cerium(IV) in Aqueous Perchloric and Sulfuric Acid Solutions: A Comparative Study

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Abstract The kinetics of the oxidation of an aminotriazole formamidine derivative, N,N-dimethyl-N′-(4H-1,2,4-triazol-3-yl) formamidine (ATF) by cerium(IV) has been studied spectrophotometrically in aqueous perchloric and sulfuric acid solutions at constant ionic strength of 1.0 mol·dm^{-3}. In both acids, the reaction shows first order kinetics with respect to [Ce(IV)], whereas the orders with respect to [ATF] are less than unity. The reaction exhibits negative fractional order kinetics with respect to [H^{+}]. The rates of reaction are not significantly affected by variations of either ionic strength or relative permittivity of the reaction's media. Addition of cerium(III) product does not affect the rates. Plausible mechanistic schemes for the reactions have been proposed. In both cases, the final oxidation products were identified as aminotriazole, dimethyl amine and carbon dioxide. Under comparable experimental conditions, the oxidation rate in perchloric acid solution is about sixfold higher than that in sulfuric acid solution. The effect of temperature on the rates has also been studied and activation parameters have been evaluated and discussed. The rate laws associated with the reaction mechanisms are derived.

Keywords Kinetics · Mechanism · Oxidation · Aminotriazole formamidine · Cerium(IV)

1 Introduction

Cerium(IV) is a powerful one electron oxidizing agent especially in acid media [1–16]. The oxidizing potentialities of cerium(IV) in sulfuric acid medium have conclusively been established [1–9]. Nevertheless, few reports on cerium(IV) oxidation in perchloric acid

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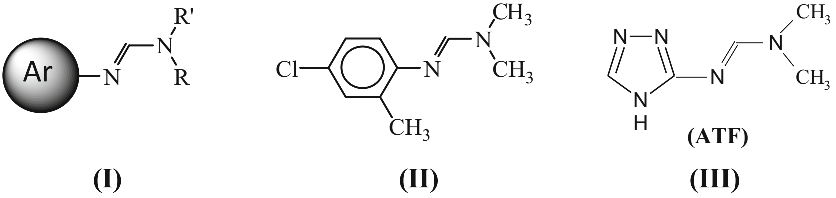


Scheme 1 Structures of some substituted formamidines

media are available [10–15], probably due to presence of dimers and polymers of cerium(IV) in such media [15]. However, the reactions of cerium(IV) in perchloric acid proceed much faster than those in sulfuric acid. Cerium(IV) oxidations of various substrates are found to follow different mechanisms, depending upon the acid medium used. Generally, for oxidations by cerium(IV), it is interesting to understand the different pathways of the reactions and different active forms of cerium(IV).

Tri-substituted formamidines of the general structure(**I**), shown in Scheme 1, have achieved importance in the last few decades due to their very broad spectrum of biological activity. The biochemical potentials of formamidines include monoamine oxidase inhibitors [17, 18], and adrenergic and neurochemical receptors [19, 20]. The *N,N*-dialkyl derivatives are highly effective acaricides and the most rewarding of these studies resulted in discovery of the acaricide insecticide chlordimeform, structure(**II**) in Scheme 1. The oxidative cleavage of formamidines is quite important, since the *N,N*-dialkyl formamidine group is one of the most versatile protecting groups, especially in biosynthetic applications.

A literature survey reveals that no work has been reported about the kinetics and mechanism of oxidation of aminotriazole formamidines by any oxidant. This observation prompted this investigation into the kinetics and mechanism of oxidation of one substituted aminotriazole formamidines, *N,N*-dimethyl-*N′*-(4*H*-1,2,4-triazol-3-yl) formamidine (ATF), Scheme 1, by cerium(IV) in both perchloric and sulfuric acid solutions. The objectives of the investigation are to establish optimum conditions affecting oxidation of ATF, to understand the active species of the oxidant and reductant in such solutions, to check the reactivity of ATF towards Ce(IV) in acid solutions and finally to elucidate plausible reaction mechanisms.

2 Experimental

2.1 Materials

The aminotriazole formamidine derivative (ATF) was synthesized and identified as reported elsewhere [21]. The stock solution of cerium(IV) was prepared by dissolving ceric ammonium sulfate in 1.0 mol·dm^{-3} H_2SO_4, diluted with double distilled water and kept overnight. The concentration of cerium(IV) was ascertained by titrating against standard ferrous ammonium sulfate solution using ferroin as an internal indicator. The solution of cerium(IV) was stored in a dark glass bottle and was used after 24 h, since the hydrolysis is negligible after 12 h from preparation [22]. Cerium(III) solution was prepared by dissolving cerium(III) acetate in water. Sodium perchlorate and sodium sulfate were used to vary the ionic strength in perchloric and sulfuric acid solutions, respectively. Other chemicals employed in the present work were of reagent grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water.

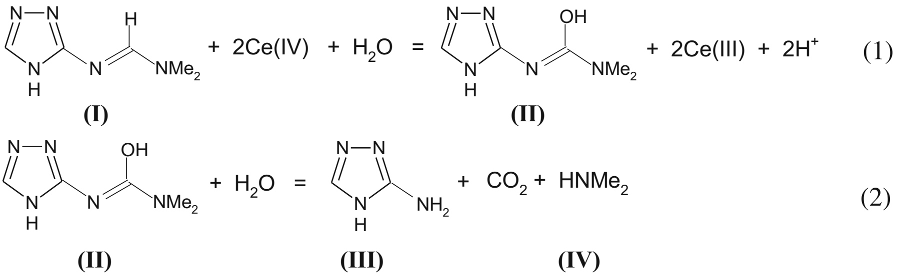
2.2 Kinetic Measurements

All kinetic runs were followed under pseudo-first order conditions with ATF in a large excess over that of cerium(IV). The progress of the reactions was followed by monitoring the decrease in absorbance of cerium(IV) as a function of time at $\lambda = 316$ nm, its absorption maximum, whereas the other constituents of the reaction mixtures do not absorb significantly at this wavelength. The applicability of Beer's law for cerium(IV) at 316 nm has been verified, giving $\varepsilon = 4362 \pm 26\ \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ in agreement with earlier reports [11, 12]. The absorbance measurements were made in a thermostatted quartz cell of a path length of 1 cm, on a Shimadzu UV–VIS–NIR-3600 double-beam spectrophotometer. First order plots of ln (absorbance) versus time were found to be good straight lines and the observed first order rate constant values (k_{obs}) were calculated as the gradients of these plots. The rate constants were reproducible to within 4 % and are the average of at least three independent kinetic runs. The reaction orders (n) with respect to the reactants in both acid solutions were determined from the slopes of $\log_{10} k_{\text{obs}}$ versus $\log_{10} (C)$ plots by varying the concentrations (C) of substrate and acids, in turn, while keeping other conditions constant. The in situ H^+ concentration in sulfuric acid–sulfate medium was calculated by using known ionization constant [23]. In the case of perchloric acid solutions, $[H^+]$ was maintained by adding requisite concentration of $HClO_4$ by subtracting the $[H^+]$ added due to H_2SO_4 present in cerium(IV) stock solution.

3 Results

3.1 Stoichiometry and Product Identification

Different sets of reaction mixtures containing various amounts of Ce(IV) and ATF at fixed acidity, ionic strength and temperature were allowed to react for 24 h in closed vessels for completion of reactions. The unreacted [Ce(IV)] was assayed spectrophotometrically at 316 nm as well as by titrating against standard ferrous ammonium sulfate solution. The results obtained in both media indicated that two moles of Ce(IV) are consumed by one mole of ATF to yield the oxidation products as shown in Scheme 2:



Scheme 2 Stoichiometric equations for the oxidation of ATF by Ce(IV) in acid solutions

where the compounds (I), (II), (III) and (IV) are ATF, 1,1-dimethyl-2-hydroxy-3-(4*H*-1,2,4-triazol-3-yl) formamidine as an intermediate product, aminotriazole and dimethylamine, respectively. The above stoichiometric equations are consistent with the results of product identification as described elsewhere [21]. Aminotriazole and dimethyl amine were identified by liquid chromatography and spot tests [24], respectively, and carbon dioxide by lime water.

3.2 Spectral Changes

The spectral changes for the oxidation of aminotriazole formamidine by cerium(IV) in both perchloric and sulfuric acid solutions are shown in Fig. 1a, b, respectively. In both cases, the scanned spectra show a gradual disappearance of the Ce(IV) band at its absorption maximum with time as a result of its reduction to Ce(III). It can be observed that the decay of Ce(IV) during the oxidation reaction carried out in perchloric acid solution is significantly faster than that in sulfuric acid solution.

3.3 Effect of [Ce(IV)]

The oxidant Ce(IV) was varied in both reactions in the range of (0.5–6.0) $\times$ 10^{-4} mol·dm^{-3} keeping other variables constant. It has been observed that the increase in the oxidant concentration does not alter the values of the rate constants (Table 1). Also, the plots of ln (absorbance) versus time plots were found to be good straight lines. These results indicate that the order of reactions with respect to the oxidant concentration is confirmed to be one.

3.4 Effect of [ATF]

The observed rate constants were determined at different initial concentrations of the reductant ATF while other variables were kept constant. It was found that increasing [ATF] increases the rates (Table 1). Plots of the observed rate constants versus [ATF] at constant

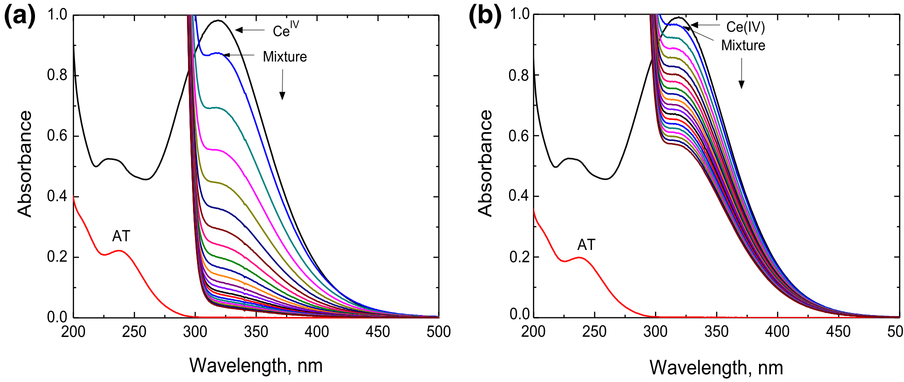


Fig. 1 Spectral changes during oxidation of ATF by Ce(IV) in: **a** perchloric acid, and **b** sulfuric acid solutions: [ATF] = 6.0 $\times$ 10^{-3}, [Ce(IV)] = 2.0 $\times$ 10^{-4}, [H$^+$] = 0.5 and I = 1.0 mol·dm^{-3} at 293.2 K; scan time intervals are 1 min

Table 1 Effect of [Ce(IV)], [ATF] and [H^+] on k_{obs} for the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions at 293.2 K

10^4 [Ce(IV)] (mol·dm^{-3})	10^3 [ATF] (mol·dm^{-3})	[H^+] (mol·dm^{-3})	10^4 k_{obs} (s^{-1})	
			Perchloric	Sulfuric
0.5	6.0	0.5	28.8	4.7
1.0	6.0	0.5	29.3	5.1
2.0	6.0	0.5	29.0	4.9
3.0	6.0	0.5	29.7	4.8
4.0	6.0	0.5	28.7	4.9
5.0	6.0	0.5	27.9	4.7
6.0	6.0	0.5	29.4	4.9
2.0	3.0	0.5	16.2	2.8
2.0	4.0	0.5	19.4	3.5
2.0	5.0	0.5	24.3	4.1
2.0	6.0	0.5	29.0	4.9
2.0	7.0	0.5	32.5	5.5
2.0	8.0	0.5	37.1	6.4
2.0	9.0	0.5	40.9	7.3
2.0	6.0	0.2	46.1	9.6
2.0	6.0	0.3	39.9	7.5
2.0	6.0	0.4	34.2	5.8
2.0	6.0	0.5	29.0	4.9
2.0	6.0	0.6	24.9	4.2
2.0	6.0	0.7	21.5	3.7
2.0	6.0	0.8	18.5	3.4

Experimental error ± 4 %. $I = 1.0$ mol·dm^{-3}

Fig. 2 Plots of k_{obs} versus [ATF] in the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions: [Ce(IV)] = 2.0×10^{-4}, [H^+] = 0.5 and $I = 1.0$ mol·dm^{-3} at 293.2 K

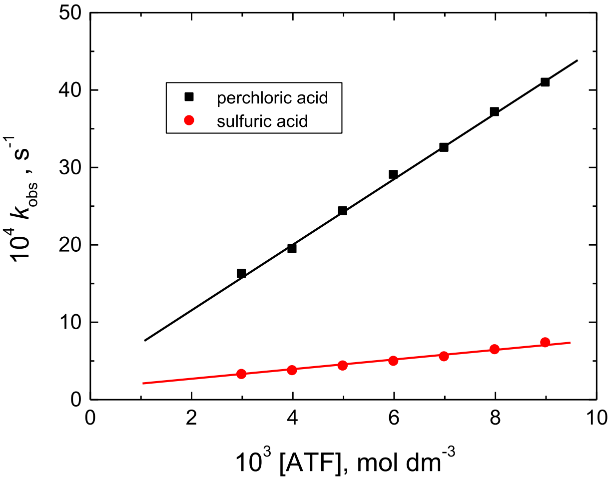
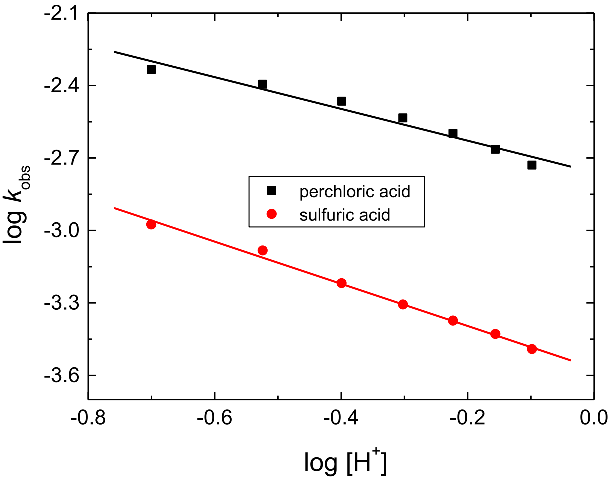


Fig. 3 Plots of $\log_{10} k_{\mathrm{obs}}$ versus $\log_{10}$ [H^+] for the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions: [ATF] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4} and I = 1.0 mol·dm^{-3} at 293.2 K



pH are linear with positive intercepts (Fig. 2), confirming the fractional order dependences with respect to [ATF] for both the acids.

3.5 Effect of [H^+]

Kinetic runs were carried out by varying the hydrogen ion concentration (0.2–0.8 mol·dm^{-3}) with perchloric acid and sulfuric acids and keeping the concentrations of all other reactants constant. It was observed that the rates of the reaction decrease with increasing [H^+] in both acids (Table 1). Plots of k_{obs} versus [H^+] are linear with negative slopes (figure not shown) confirming negative fractional-first order dependences with respect to [H^+]. Furthermore, the plots of $\log_{10} k_{\mathrm{obs}}$ versus log [H^+] were linear with slopes of −0.66 and −0.87 in perchloric and sulfuric acids, respectively, as shown in Fig. 3.

3.6 Effect of Ionic Strength and Relative Permittivity of the Acid Media

The effect of ionic strength on the rates of the reactions was studied by varying the ionic strength in the range 1.0–2.2 mol·dm^{-3} using sodium perchlorate in the case of perchloric acid and sodium sulfate in case of sulfuric acid while keeping the concentrations of all other reactants constant. The results indicate that variation of ionic strength was found to have negligible effect on the reaction rates in both cases.

The relative permittivity (ε) effect was studied by varying the acetic acid–water content in the reaction mixtures with all other conditions being kept constant. The relative permittivities were computed from the values of pure liquids by considering their values $\boldsymbol{\varepsilon}$ in pure form using equation: $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_1 \boldsymbol{V}_1 + \boldsymbol{\varepsilon}_2 \boldsymbol{V}_2$, where $\boldsymbol{V}_1$ and $\boldsymbol{V}_2$ are volume fractions and $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$ are relative permittivities of water and acetic acid as 78.5 and 6.15 at 298.15 K, respectively. The rate constants increased negligibly with decreasing relative permittivity of the acid solutions.

3.7 Effect of [HSO_4^-]

In the case of sulfuric acid, kinetic runs were carried out at different concentrations of bisulfate in the range 0.3–0.9 mol·dm^{-3}, keeping the concentrations of all other reactants

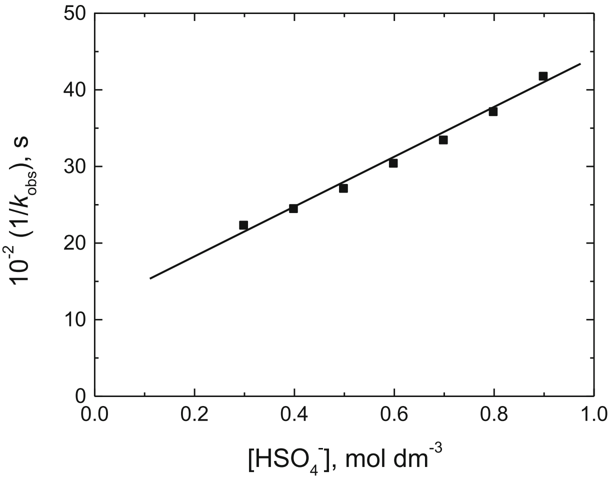


Fig. 4 A plot of $1/k_{obs}$ versus $[HSO_4^-]$ for the oxidation of ATF by Ce(IV) in sulfuric acid solution: [ATF] = 6.0×10^{-3}, [Ce(IV)] = $2. \times 10^{-4}$, $[H^+]$ = 0.5 and I = 1.0 mol·dm^{-3} at 293.2 K

constant. It was observed that increase in bisulfate concentration decreases the rate of the reaction and the order with respect to $[HSO_4^-]$ was negative. This is confirmed by the linear plot of $1/k_{obs}$ versus $[HSO_4^-]$ with positive intercept as shown in Fig. 4.

3.8 Effect of Initially Added Product

The effect of added cerium(III) product was studied in the concentration range 0.5–6.0 × 10^{-4} mol·dm^{-3} at fixed concentrations of the oxidant, reductant and acids. It was found that Ce(III) did not have any significant effect on the rates of reactions in either perchloric or sulfuric acid solutions.

3.9 Effect of Temperature

The rates of the reactions were carried out at four different temperatures: 283, 293, 303 and 313 K, at constant concentrations of the reactants and other conditions being constant. The results indicate that the pseudo-first order rate constants increase with increasing temperature. The activation parameters of the second order rate constant (k') were calculated using Arrhenius, Fig. 5a, and Eyring, Fig. 5b, plots and are listed in Table 2.

3.10 Effect of Mn^{2+} and Al^{3+} Catalysts

In both perchloric and sulfuric acid solutions, the rates of the reactions were measured at various $[Mn^{2+}]$ and $[Al^{3+}]$ (3.0–9.0 × 10^{-5} mol·dm^{-3}) with other conditions being constant. The results show that the rates increased with increase in both $[Mn^{2+}]$ and $[Al^{3+}]$ and the catalytic efficiency of Al^{3+} was higher than that of Mn^{2+} as shown in Figs. 6 and 7.

3.11 Test for Free Radical Intermediates

It is well known [1–6, 9–11] that cerium(IV) is a generator of free radicals, due to its single equivalent change in redox reactions. Hence, the intervention of free radicals during the reactions was examined as follows. The reaction mixtures, to which known quantities of

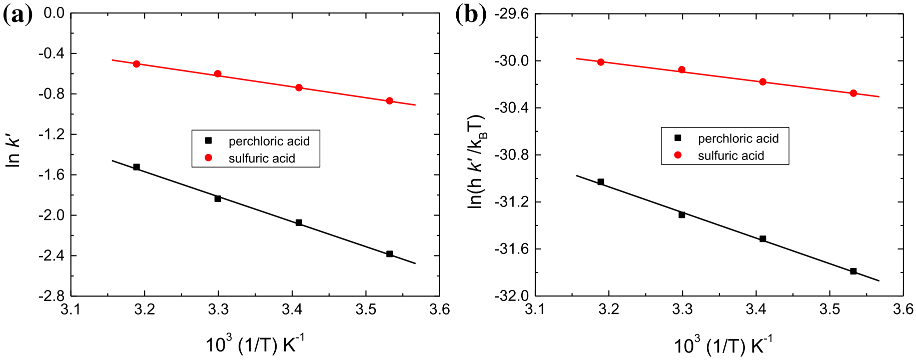


Fig. 5 **a** Arrhenius and, **b** Eyring plots in the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions: [ATF] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 0.5 and $I = 1.0$ mol·dm^{-3}

Table 2 Activation parameters of the second order rate constants *k'* for the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions

Reaction	$\Delta S^{\neq}$ (J·mol^{-1}·K^{-1})	$\Delta H^{\neq}$ (kJ·mol^{-1})	$\Delta G^{\neq}_{298}$ (kJ·mol^{-1})	$E^{\neq}_{a}$ (kJ·mol^{-1})
Perchloric acid	−194.54	18.12	75.12	20.55
Sulfuric acid	−223.82	6.48	71.76	9.04

[ATF] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 0.5 and $I = 1.0$ mol·dm^{-3}. Experimental error ± 3 %

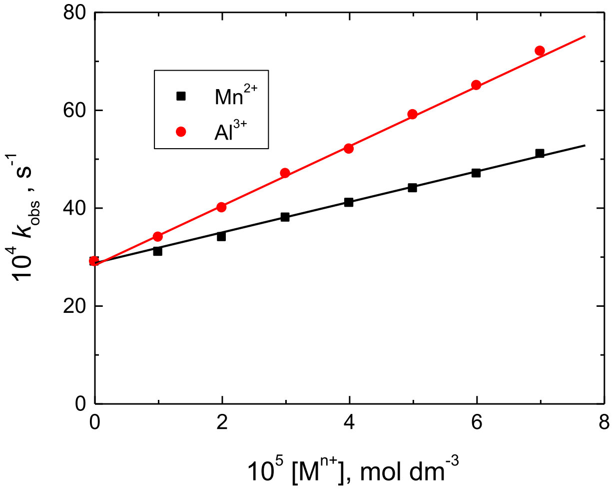


Fig. 6 Effect of [Mn^{2+}] and [Al^{3+}] on k_{obs} in the oxidation of ATF by Ce(IV) in perchloric acid solution: [ATF] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 0.5 and $I = 1.0$ mol·dm^{-3} at 293.2 K

acrylonitrile scavenger have been added initially, were kept in inert atmosphere for 2 h. Upon diluting the reaction mixtures with methanol, white precipitates formed, implying the generation of free radicals in the reactions. When the experiments were repeated in the absence of ATF under similar conditions, the tests were negative. This indicates that the reactions were routed through free radical paths.

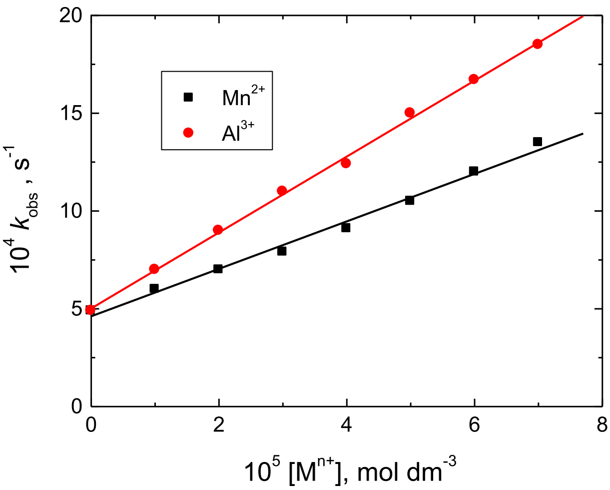


Fig. 7 Effect of [Mn^{2+}] and [Al^{3+}] on k_{obs} in the oxidation of ATF by Ce(IV) in sulfuric acid solution: [ATF] = 6.0×10^{-3}, [Ce(IV)] = 2.0×10^{-4}, [H^+] = 0.5 and $I = 1.0$ mol·dm^{-3} at 293.2 K

4 Discussion

4.1 Kinetically Active Cerium(IV) Species in Acid Solutions

A survey on the earlier literature on the nature of cerium(IV) species in perchloric acid solution [25–27] showed that the active species of cerium(IV) was found to be either free monomeric species Ce^{4+}, its hydrolyzed forms, $Ce(OH)^{3+}$ and $Ce(OH)_2^{2+}$, or partially in the form of dimeric species $(Ce–O–Ce)^{6+}$ and $(HOCe–O–CeOH)^{4+}$. However, Offiner and Skoog [28] showed from the spectrophotometric studies that the hydrated form, Ce^{4+}, is the predominant species at $[H^+] \geq 1.0$ mol·dm^{-3} for Ce(IV) concentrations up to 1.5×10^{-3} mol·dm^{-3}, whereas the hydrolyzed forms and dimers are predominant at $[H^+] < 0.8$ mol·dm^{-3}. Therefore, under our experimental conditions of low [H^+] and deceasing reaction rate with increasing [H^+], $Ce(OH)^{3+}$ may be regarded as the kinetically active form of cerium(IV) according to the following equilibria:

$$Ce^{4+} + H_2O \overset{K_{OH}}{\rightleftharpoons} Ce(OH)^{3+} + H^+.$$

In sulfuric acid medium [1–9], and depending upon the concentrations of H^+, HSO_4^- and H_2SO_4, Ce(IV) forms several sulfate complexes such as $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$ and $HCe(SO_4)_4^-$, although their role has not received much attention. Based on the effects of [H^+] and [HSO_4^-] on the rate of the reaction, one or other of these species were treated to be the kinetically active species of cerium(IV). The following equilibria [29] lead to the formation of sulfato complexes of cerium(IV):

$$Ce^{4+} + SO_4^{2-} \overset{K_1}{\rightleftharpoons} Ce(SO_4)^{2+} \quad (A)$$

$$CeSO_4^{2+} + SO_4^{2-} \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 \quad (B)$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} HCe(SO_4)_3^- \quad (C)$$

$$HCe(SO_4)_3^- + HSO_4^- + H^+ \overset{K_4}{\rightleftharpoons} HCe(SO_4)_4^- \quad (D)$$

The observations that both H^+ and HSO_4^- ions retard the rate of oxidation point to the fact that $HCe(SO_4)_3^-$ (equilibrium D) may be considered as the kinetically active species, which shows parallels with variations of k_{obs} with both [H^+] and [HSO_4^-] in the present investigation as shown in Figs. 3 and 4. As the sulfuric acid concentration increases both the [H^+] and [HSO_4^-] also increase. If the rate is inversely dependent on the [HSO_4^-] to a great extent then the overall effect of adding sulfuric acid would lower the rate as obtained experimentally (Table 1). Similar behavior has been reported elsewhere [29].

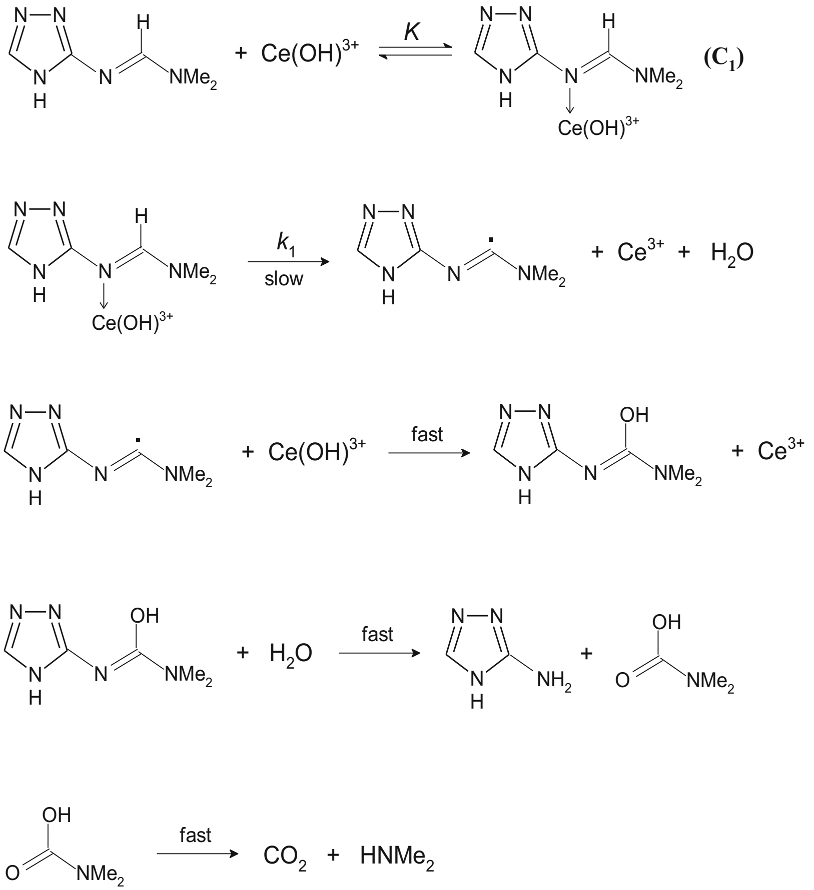
4.2 Reaction Mechanism

The reactions between ATF and Ce(IV) in both perchloric and sulfuric acid media have a stoichiometry of 1:2, i.e., one mole of ATF requires two moles of Ce(IV). The reactions exhibit first order dependence with respect to [Ce(IV)], less than unit orders with respect to [ATF] and negative fractional orders in [H^+]. The rate is not significantly affected by Ce(III), ruling out the probability of any fast equilibrium with the product, preceding the rate-determining step. The rate-determining step should be irreversible as is generally the case for one electron oxidants [30] and the oxidation takes place through generation of free radicals as found experimentally. The rates of reaction are not significantly affected by variation of either ionic strength or relative permittivity of the reactions medium, suggesting that the reactions occur between a neutral molecule and charged ions [31, 32].

The less than unit orders with respect to [ATF] presumably result from formation of complexes between the different Ce(IV) species and ATF prior to the rate-determining steps. Complexes formation was proved kinetically by the non-zero intercepts of the plots of $1/k_{obs}$ versus 1/[ATF] (Fig. 8) in favor of possible formation of an intermediate complex between the oxidant and substrate, similar to the well-known Michaelis–Menten [33] mechanism for enzyme–substrate reactions. The failure of the spectrophotometric detection of such intermediate complexes (Fig. 1) may be interpreted by either lower concentrations of the reactants used and, hence, the expected lower absorbitivities of the formed complexes and/or the fast subsequent decomposition of the intermediates in comparison with their formation. The complexes formed were slowly decomposed in the rate-determining steps to give rise to the initial oxidation products as the substrate radical (ATF·) and Ce(III). The substrate radical reacts with another Ce(IV) species in a subsequent fast step to yield an intermediate product, 1,1-dimethyl-2-hydroxy-3-(4*H*-1,2,4-triazol-3-yl) formamidine (or 1,1-dimethyl-3-(4*H*-1,2,4-triazol-3-yl) urea). In a further fast step, the intermediate product is hydrolyzed to give the final oxidation products, as given in Schemes 3 and 4 for reactions in perchloric and sulfuric acids, respectively. Since such Schemes are in accordance with the generally accepted principle of non-complementary oxidations taking place in a sequence of one-electron steps, the reaction between the substrate and oxidant would afford radical intermediates as was observed.

4.2.1 Reaction Mechanism in Perchloric Acid Solution

$$Ce^{4+} + H_2O \overset{K_{OH}}{\rightleftharpoons} Ce(OH)^{3+} + H^+ \tag{3}$$



(4)
(5)
(6)
(7)
(8)

Scheme 3 Mechanism of oxidation of ATF by Ce(IV) in perchloric acid solution

The suggested mechanism leads to the following rate law (see Appendix 1),

$$\text{Rate} = \frac{k_1 K_{\text{OH}} K[\text{Ce(IV)}][\text{ATF}]}{[\text{H}^+] + K_{\text{OH}} + K_{\text{OH}} K[\text{ATF}]} \tag{9}$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. 10,

$$\text{Rate} = \frac{-\text{d}[\text{Ce(IV)}]}{\text{d}t} = k_{\text{obs}}[\text{Ce(IV)}] \tag{10}$$

Comparing Eqs. 9 and 10, the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_1 K_{\text{OH}} K[\text{ATF}]}{[\text{H}^+] + K_{\text{OH}} + K_{\text{OH}} K[\text{ATF}]} \tag{11}$$

The rate law (Eq. 9) is consistent with all the observed orders with respect to different species, which can be verified by rearranging to the following equations:

$$\frac{1}{k_{\text{obs}}} = \left(\frac{[\text{H}^+] + K_{\text{OH}}}{k_1 K_{\text{OH}} K}\right)\frac{1}{[\text{ATF}]} + \frac{1}{k_1} \tag{12}$$

Fig. 8 Plots of $1/k_{obs}$ versus $1/[ATF]$ in the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions: $[Ce(IV)] = 2.0 \times 10^{-4}$, $[H^+] = 0.5$ and $I = 1.0\ mol{\cdot}dm^{-3}$ at 293.2 K

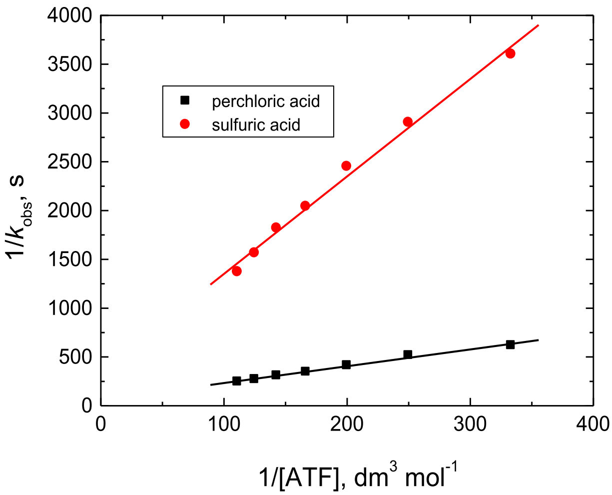
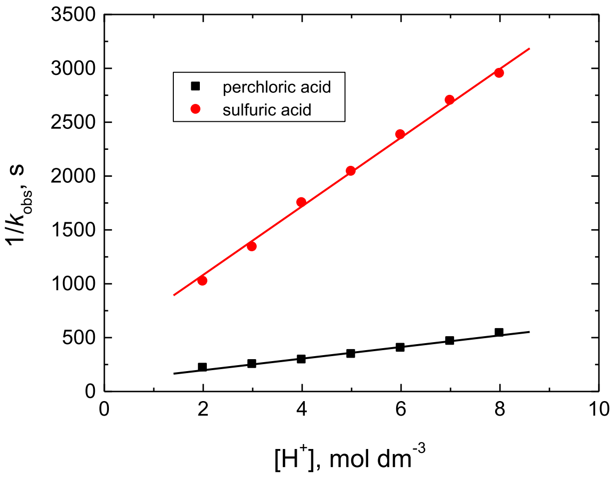


Fig. 9 Plots of $1/k_{obs}$ versus $[H^+]$ in the oxidation of ATF by Ce(IV) in perchloric and sulfuric acid solutions: $[ATF] = 6 \times 10^{-3}$, $[Ce(IV)] = 2.0 \times 10^{-4}$ and $I = 1.0\ mol{\cdot}dm^{-3}$ at 20 293.2 K

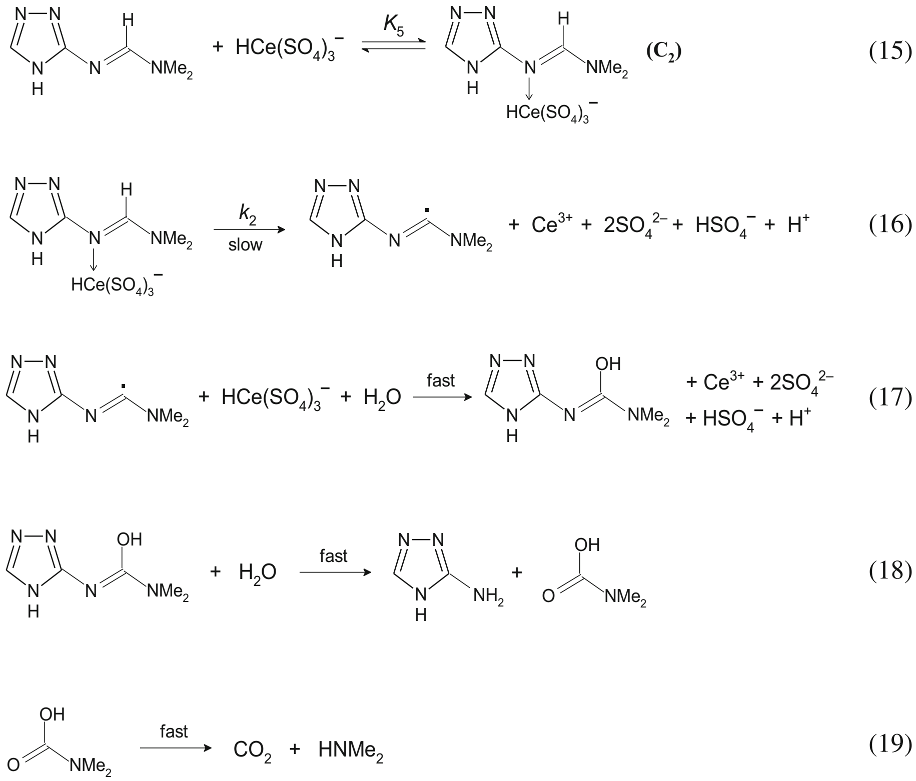


$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_{OH} K[ATF]}\right)[H^+] + \frac{1}{k_1 K[ATF]} + \frac{1}{k_1} \tag{13}$$

According to Eqs. 12 and 13, plots of $1/k_{obs}$ versus $1/[ATF]$ at constant $[H^+]$, and $1/k_{obs}$ versus $[H^+]$ at constant [ATF] should be linear with positive intercepts and are found to be so as shown in Figs. 8 and 9, respectively. From the slopes and intercepts of these plots the obtained values of k_1, K_{OH}, and K are $13.11 \times 10^{-3}\ s^{-1}$, $0.27\ mol{\cdot}dm^{-3}$, and $854.69\ dm^3{\cdot}mol^{-1}$, respectively, at 293.2 K.

4.2.2 *Reaction Mechanism in Sulfuric Acid Medium*

$$HCe(SO_4)_3^- + HSO_4^- + H^+ \overset{K_4}{\rightleftharpoons} H_3Ce(SO_4)_4^- \tag{14}$$



Scheme 4 Mechanism of oxidation of ATF by Ce(IV) in sulfuric acid solution

The suggested mechanism leads to the following rate law (see Appendix 2):

$$\text{Rate} = \frac{k_2 K_5 [\text{Ce(IV)}][\text{ATF}]}{1 + K_4[\text{HSO}_4^-][\text{H}^+] + K_5[\text{ATF}]} \tag{20}$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. 21:

$$\text{Rate} = \frac{-\text{d}[\text{Ce(IV)}]}{\text{d}t} = k_{\text{obs}}[\text{Ce(IV)}] \tag{21}$$

Comparing Eqs. 20 and 21, the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_2 K_5 [\text{ATF}]}{1 + K_4[\text{HSO}_4^-][\text{H}^+] + K_5[\text{ATF}]} \tag{22}$$

The rate law (Eq. 22) is consistent with all the observed orders with respect to different species, which can be verified by rearranging to Eqs. 23 and 24:

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K_4[\text{HSO}_4^-][\text{H}^+]}{k_2 K_5}\right)\frac{1}{[\text{ATF}]} + \frac{1}{k_2} \tag{23}$$

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{K_4}{k_2 K_5}\right)[\mathrm{HSO_4^-}][\mathrm{H^+}] + \frac{1}{k_2 K_5[\mathrm{ATF}]} + \frac{1}{k_2} \qquad (24)$$

Thus, the plots of $1/k_{\mathrm{obs}}$ versus 1/[ATF] at constant $[\mathrm{H^+}]$, and $1/k_{\mathrm{obs}}$ versus $[\mathrm{H^+}]$ at constant [ATF] should be linear with positive intercepts and are found to be so as shown also in Figs. 8 and 9, respectively. From the slopes and intercepts of these plots the obtained values of k_2, K_4, and K_5 are $3.09 \times 10^{-3}\ \mathrm{s^{-1}}$, 563.88 $\mathrm{dm^6{\cdot}mol^{-2}}$, and 336.01 $\mathrm{dm^3{\cdot}mol^{-1}}$, respectively, at 293.2 K.

The obtained activation parameters listed in Table 2 can be discussed as follows. The negative values of ΔS suggest interaction of reacting ions of similar charges to form intermediate complexes of inner-sphere nature [34, 35]. These values are within the range of radical reactions and have been ascribed to the nature of the electron pairing and unpairing process and to the loss of degree of freedom formerly available to the reactants upon formation of a rigid transition state [36, 37]. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are both favorable for electron transfer processes. On the other hand, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate endothermic formation of the complexes.

The enhancement of oxidation rate upon addition of the metal cations $\mathrm{Mn^{2+}}$ and $\mathrm{Al^{3+}}$ can be interpreted by one of several paths, such as formation of complexes with the reactants, oxidation of the substrate itself or through the formation of free radicals [38–40].

5 Conclusion

A comparative study of oxidation of one of aminotriazole formamidine derivatives, namely *N,N*-dimethyl-*N*′-(4*H*-1,2,4-triazol-3-yl) formamidine by cerium(IV) in aqueous perchloric and sulfuric acid solutions was performed. The rate of oxidation in perchloric acid solution is about sixfold faster than that observed in sulfuric acid solution. Under our experimental conditions, $\mathrm{Ce(OH)^{3+}}$ and $\mathrm{HCe(SO_4)_3^-}$ may be regarded as the active forms of cerium(IV) in perchloric and sulfuric acid solutions, respectively.

Appendix 1

Derivation of rate law in the case of perchloric acid.

According to the suggested mechanism and regarding to reaction (5),

$$\mathrm{Rate} = \frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = k_1[\mathrm{C_1}] \qquad (25)$$

Regarding to reactions (3) and (4),

$$K_{\mathrm{OH}} = \frac{[\mathrm{Ce(OH)^{3+}}][\mathrm{H^+}]}{[\mathrm{Ce^{4+}}]}, \quad [\mathrm{Ce(OH)^{3+}}] = \frac{K_{\mathrm{OH}}[\mathrm{Ce^{4+}}]}{[\mathrm{H^+}]} \qquad (26)$$

and

$$K = \frac{[C_1]}{[\mathrm{Ce(OH)^{3+}}][\mathrm{ATF}]}, \quad [C_1] = K[\mathrm{Ce(OH)^{3+}}][\mathrm{ATF}] = \frac{K_{\mathrm{OH}}K[\mathrm{Ce^{4+}}][\mathrm{ATF}]}{[\mathrm{H^+}]} \qquad (27)$$

Substituting Eq. 27 into Eq. 25 leads to,

$$\text{Rate} = \frac{k_1 K_{\text{OH}} K[\text{Ce}^{4+}][\text{ATF}]}{[\text{H}^+]} \tag{28}$$

The total concentration of ATF is given by:

$$[\text{ATF}]_{\text{T}} = [ATF]_{\text{F}} + [C_1] \tag{29}$$

where ‘T’ and ‘F’ stand for total and free concentrations.

Substituting Eq. 27 into Eq. 29 and rearrangement gives,

$$[\text{ATF}]_{\text{T}} = [\text{ATF}]_{\text{F}} + \frac{K_{\text{OH}} K[\text{Ce}^{4+}][\text{ATF}]}{[\text{H}^+]} \tag{30}$$

$$[\text{ATF}]_{\text{T}} = [\text{ATF}]_{\text{F}} \left(1 + \frac{K_{\text{OH}} K[\text{Ce}^{4+}]}{[\text{H}^+]}\right) \tag{31}$$

Therefore,

$$[\text{ATF}]_{\text{F}} = \frac{[\text{ATF}]}{1 + \frac{K_{\text{OH}} K[\text{Ce}^{4+}]}{[\text{H}^+]}} \tag{32}$$

In view of low [Ce^{4+}], the second denominator term $K_{\text{OH}}K[\text{Ce}^{4+}]/[\text{H}^+]$ in the above equation is neglected. Therefore,

$$[\text{ATF}]_{\text{F}} = [\text{ATF}]_{\text{T}} \tag{33}$$

Also,

$$[\text{Ce(IV)}]_{\text{T}} = [\text{Ce}^{4+}]_{\text{F}} + [\text{Ce(OH)}^{3+}] + [C_1] \tag{34}$$

Substituting Eqs. 26 and 27 into Eq. 34,

$$[\text{Ce(IV)}]_{\text{T}} = [\text{Ce}^{4+}]_{\text{F}} + \frac{K_{\text{OH}}[\text{Ce}^{4+}]}{[\text{H}^+]} + \frac{K_{\text{OH}} K[\text{Ce}^{4+}][\text{ATF}]}{[\text{H}^+]} \tag{35}$$

$$[\text{Ce(IV)}]_{\text{T}} = [\text{Ce}^{4+}]_{\text{F}} \left(1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \frac{K_{\text{OH}} K[\text{ATF}]}{[\text{H}^+]}\right) \tag{36}$$

$$[\text{Ce}^{4+}]_{\text{F}} = \frac{[\text{Ce(IV)}]_T}{1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \frac{K_{\text{OH}} K[\text{ATF}]}{[\text{H}^+]}} \tag{37}$$

Substituting Eqs. 33 and 37 into Eq. 28 (and omitting ‘T’ and ‘F’ subscripts) leads to,

$$\text{Rate} = \frac{k_1 K_{\text{OH}} K[\text{Ce(IV)}][\text{ATF}]}{1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \frac{K_{\text{OH}} K[\text{ATF}]}{[\text{H}^+]}} = \frac{k_1 K_{\text{OH}} K[\text{Ce(IV)}][\text{ATF}]}{[\text{H}^+] + K_{\text{OH}} + K_{\text{OH}} K[\text{ATF}]} \tag{38}$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. 39,

$$\text{Rate} = \frac{-\text{d}[\text{Ce(IV)}]}{\text{d}t} = k_{\text{obs}}[\text{Ce(IV)}] \tag{39}$$

Comparing Eqs. 38 and 39, the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_1 K_{\text{OH}} K[\text{ATF}]}{[\text{H}^+] + K_{\text{OH}} + K_{\text{OH}} K[\text{ATF}]} \tag{40}$$

and with rearrangement, the following equations are obtained,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{[H^+] + K_{\text{OH}}}{k_1 K_{\text{OH}} K_1}\right) \frac{1}{[\text{ATF}]} + \frac{1}{k_1} \tag{41}$$

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{k_1 K_{\text{OH}} K_1 [\text{ATF}]}\right)[\text{H}^+] + \frac{1}{k_1 K_1 [\text{ATF}]} + \frac{1}{k_1}. \tag{42}$$

Appendix 2

Derivation of rate law in case of sulfuric acid.

According to the suggested mechanism and regarding to reaction (16),

$$\text{Rate} = \frac{-\text{d}[\text{Ce(IV)}]}{\text{d}t} = k_2[C_2] \tag{43}$$

Regarding reactions (14) and (15),

$$K_4 = \frac{[\text{H}_3\text{Ce}(\text{SO}_4)_4^-]}{[\text{HCe}(\text{SO}_4)_3^-][\text{HSO}_4^-][\text{H}^+]}, \quad [\text{H}_3\text{Ce}(\text{SO}_4)_4^-] = K_4[\text{HCe}(\text{SO}_4)_3^-][\text{HSO}_4^-][\text{H}^+] \tag{44}$$

$$K_5 = \frac{[C_2]}{[\text{HCe}(\text{SO}_4)_3^-][\text{ATF}]}, \quad [C_2] = K_5[\text{HCe}(\text{SO}_4)_3^-][\text{ATF}] \tag{45}$$

Substituting Eq. 45 into Eq. 43 leads to,

$$\text{Rate} = k_2 K_5 [\text{HCe}(\text{SO}_4)_3^-][\text{ATF}] \tag{46}$$

The total concentration of ATF is given by:

$$[\text{ATF}]_{\text{T}} = [\text{ATF}]_{\text{F}} + [C_2] \tag{47}$$

Substituting Eq. 45 into Eq. 47 and rearrangement gives,

$$[\text{ATF}]_{\text{T}} = [\text{ATF}]_{\text{F}} + K_5[\text{HCe}(\text{SO}_4)_3^-][\text{ATF}] \tag{48}$$

$$[\text{ATF}] = [\text{ATF}]_{\text{F}}(1 + K_5[\text{HCe}(\text{SO}_4)_3^-]) \tag{49}$$

Therefore,

$$[\text{ATF}]_{\text{F}} = \frac{[\text{ATF}]_{\text{T}}}{1 + K_5[\text{HCe}(\text{SO}_4)_3^-]} \tag{50}$$

In view of low $[\text{HCe}(\text{SO}_4)_3^-]$, the second numerator term in the above equation is neglected. Therefore,

$$[\text{ATF}]_{\text{F}} = [\text{ATF}]_{\text{T}} \tag{51}$$

Also,

$$[\mathrm{Ce(IV)}]_{\mathrm{T}} = [\mathrm{HCe(SO_4)_3^-}] + [\mathrm{H_3Ce(SO_4)_4^-}] + [C_2] \tag{52}$$

Substituting Eqs. 44 and 45 into Eq. 52,

$$[\mathrm{Ce(IV)}]_{\mathrm{T}} = [\mathrm{HCe(SO_4)_3^-}] + K_4[\mathrm{HCe(SO_4)_3^-}][\mathrm{HSO_4^-}][\mathrm{H^+}] + K_5[\mathrm{HCe(SO_4)_3^-}][\mathrm{ATF}] \tag{53}$$

$$[\mathrm{Ce(IV)}]_{\mathrm{T}} = [\mathrm{HCe(SO_4)_3^-}](1 + K_4[\mathrm{HSO_4^-}][\mathrm{H^+}] + K_5[\mathrm{ATF}]) \tag{54}$$

$$[\mathrm{HCe(SO_4)_3^-}] = \frac{[\mathrm{Ce(IV)}]_{\mathrm{T}}}{1 + K_4[\mathrm{HSO_4^-}][\mathrm{H^+}] + K_5[\mathrm{ATF}]} \tag{55}$$

Substituting Eqs. 51 and 55 into Eq. 46 leads to,

$$\mathrm{Rate} = \frac{k_2K_5[\mathrm{Ce(IV)}][\mathrm{ATF}]}{1 + K_4[\mathrm{HSO_4^-}][\mathrm{H^+}] + K_5[\mathrm{ATF}]} \tag{56}$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. 57,

$$\mathrm{Rate} = \frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{Ce(IV)}] \tag{57}$$

Comparing Eqs. 56 and 57, the following relationship is obtained,

$$k_{\mathrm{obs}} = \frac{k_2K_5[\mathrm{ATF}]}{1 + K_4[\mathrm{HSO_4^-}][\mathrm{H^+}] + K_5[\mathrm{ATF}]} \tag{58}$$

and with rearrangement, the following equations are obtained:

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{1 + K_4[\mathrm{HSO_4^-}][\mathrm{H^+}]}{k_2K_5}\right)\frac{1}{[\mathrm{ATF}]} + \frac{1}{k_2} \tag{59}$$

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{K_4}{k_2K_5}\right)[\mathrm{HSO_4^-}][\mathrm{H^+}] + \frac{1}{k_2K_5[\mathrm{ATF}]} + \frac{1}{k_2}. \tag{60}$$

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