Kinetics and Mechanistic Study of Oxidation of Pyridine Derivative by Cerium(IV) in Aqueous Perchloric Acid

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To cite this article:
Ahmed Fawzy, Ishaq A. Zaafarany, Fahd A. Tirkistani, Ameena Al-Bonayan, Faten A. Aljiffrey. Kinetics and Mechanistic Study of Oxidation of Pyridine Derivative by Cerium(IV) in Aqueous Perchloric Acid. *American Journal of Physical Chemistry.* Vol. 5, No. 1, 2016, pp. 10-16. doi: 10.11648/j.ajpc.20160501.12

Abstract: The kinetics of oxidation of *N, N*-dimethyl-*N'*-(pyridin-2-yl) formamidine (Py-F) by cerium(IV) was studied spectrophotometrically in aqueous perchloric acid solutions at a constant ionic strength of 1.0 mol dm^{-3} and at 20°C. The reaction showed first order dependence with respect to [Ce(IV)] and less than unit order with respect to [Py-F]. The reaction exhibited negative fractional-first order kinetics with respect to [H$^+$]. The rate of reaction was not significantly affected by variation of either ionic strength or dielectric constant of the reaction medium. Addition of cerium(III) product did not affect the reaction rate. A suitable mechanistic scheme for the oxidation reaction has been proposed. The final oxidation products were identified as 2-aminopyridine, dimethylamine and carbon dioxide. The activation parameters have been evaluated and discussed. The rate law associated with the reaction mechanism was derived.

Keywords: Kinetics, Mechanism, Oxidation, Pyridine Derivative, Cerium(IV)

1. Introduction

Aminopyridine is an important organic compound which is used in the production of the drugs piroxicam, sulfa pyridine, tenoxicam, and tripelennamine. Also, substituted formamidines have achieved considerable significance during the last few decades [1-4] due to their very broad spectrum of biological activity. The biochemical potentialities of formamidines include monoamine oxidase inhibitors [1, 2], adrenergic and neurochemical receptors [3, 4]. The *N, N*-dialkyl derivatives are highly effective acaricides and the most rewarding of these studies resulted in the discovery of acaricide insecticide chlordimeform. 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.

Cerium(IV) is a powerful one electron oxidizing agent in acid media [5-20]. Oxidation by cerium(IV) in sulfuric acid solutions have conclusively been established [5-13]. Nevertheless, little reports on cerium(IV) oxidation in perchloric acid solutions [14-19], probably due to presence of

dimers and polymers of cerium(IV) in such solutions [19]. However, the reactions of cerium(IV) in perchloric acid medium proceed much faster than those in sulfuric acid medium. Cerium(IV) oxidations of various substrates are found to follow different mechanisms, depending upon the acid medium used. Such oxidation are generally interesting to understand the different pathways of the reactions and different active forms of cerium(IV).

No work has been reported about the kinetics and mechanism of oxidation of pyridine derivatives by cerium(IV). This observation prompted us to investigate the title reaction. We aim to establish the optimum conditions affecting oxidation of *N, N*-dimethyl-*N'*-(pyridin-2-yl) formamidine (Py-F) by cerium(IV) in perchloric acid solutions, to understand the kinetically active species of Ce(IV) and finally to elucidate a plausible oxidation mechanism.

2. Experimental

2.1. Materials

All 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. The stock solution of Py-F was prepared as reported elsewhere [21]. Cerium(IV) solution was freshly prepared by dissolving ceric ammonium sulfate in a 1.0 mol dm^{-3} sulfuric acid, diluted with double distilled water and kept for overnight. 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 small or ruled out after 12 h of preparation [22]. Cerium(III) solution was prepared by dissolving cerium(III) acetate in water.

2.2. Kinetic Measurements

Kinetic measurements were followed under pseudo-first order conditions where Py-F was present in a large excess over that of cerium(IV). The progress of the reaction was followed by monitoring the decrease in absorbance of cerium(IV) as a function of time at λ = 316 nm, its absorption maximum, whereas the other constituents of the reaction mixture do not absorb significantly at this wavelength. The applicability of Beer's law for cerium(IV)at 315 nm has been verified giving ε = 4371 ± 28 dm^3 mol^{-1} cm^{-1} in agreement with the earlier reports [15, 16]. The absorbance measurements were made in a thermostatted quartz cell of a pathlength 1.0 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 such plots. The rate constants were reproducible to within 4% and were the average of at least two independent kinetic runs. The effect of dissolved oxygen on the reaction rate was checked by monitoring the reaction in a nitrogen atmosphere. No significant difference between the results obtained under nitrogen and in the presence of air was observed.
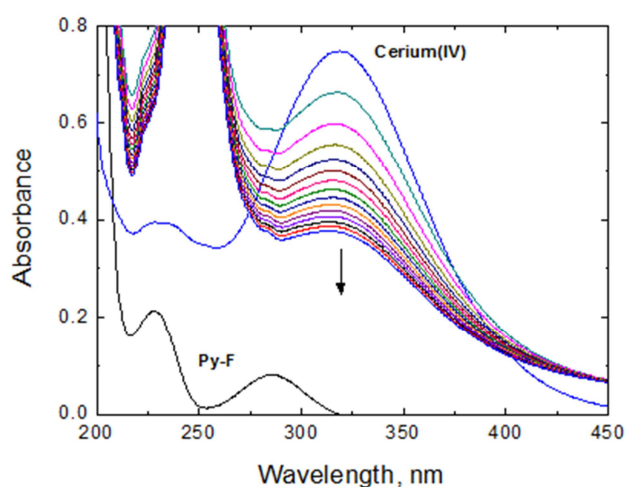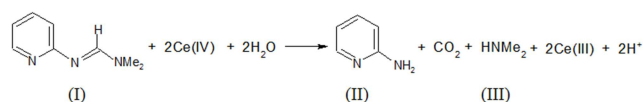

Figure 1. *Time-resolved spectra during oxidation of Py-F by Ce(IV) in perchloric acid solution. [Py-F] = 8.0 x 10^{-3}, [Ce(IV)] = 2.0 x 10^{-4}, [H^+] = 0.3 and I = 1.0 dm^{-3} at 25°C. Scanning time intervals = 8 min.*

Time-resolved spectra during the oxidation of Py-F by Ce(IV) in aqueous perchloric acid solutions are shown in Figure 1. The scanned spectra indicate gradual disappearance of Ce(IV) band at its absorption maximum with time as a result of its reduction to Ce(III).

3. Results

3.1. Stoichiometry and Product Analysis

Reaction mixtures containing various amounts of Ce(IV) and Py-F at constant [H^+], 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 315 nm as well as by titrating against standard ferrous ammonium sulfate solution. The results indicated that two moles of Ce(IV) were consumed by one mole of Py-F yielding the oxidation products as shown in the following equation,

where the compounds (I), (II) and (III) are *N, N*-dimethyl-*N'*-(pyridin-2-yl) formamidine (Py-F), 2-aminopyridine and dimethylamine, respectively. The above stoichiometric equation is consistent with the results of product analysis as described elsewhere [21]. 2-Aminopyridine and dimethylamine were identified by liquid chromatography and spot tests [24], respectively, and CO_2 by lime water.

3.2. Reaction Order with Respect to the Reactants

The reaction orders (n) with respect to the different reactants were determined from the slopes of log k_{obs} versus log(concentration) plots by varying the concentrations (C) of substrate and acid, in turn, while keeping other conditions constant.

The oxidant, cerium(IV) was varied in the range of (0.5 - 5.0) x 10^{-4} mol dm^{-3} keeping other variables constant. It has been observed that the increase in the oxidant concentration did not alter the rate constant value (Table 1). Also, the plots of ln(absorbance) versus time were found to be good straight lines. These results indicate that the order of reaction with respect to the oxidant concentration is confirmed to be one.

The observed rate constant was determined at different initial [Py-F] while other variables were kept constant. Increasing [Py-F] increased the reaction rate as listed in Table 1. A plot of the k_{obs} versus [Py-F] at constant pH is linear with a positive intercept as shown in Figure 2 confirming fractional-first order dependence with respect to [Py-F].

Kinetic runs were carried out by varying the hydrogen ion concentration (0.1–0.9 mol dm^{-3}) and keeping the concentrations of all other reactants constant. It was observed that the rate of the reaction decreased with increasing [H^+] (Table 1). A plot of k_{obs} versus [H^+] was linear with a negative slope (Figure 3) confirming negative fractional-first order dependence with respect to [H^+].

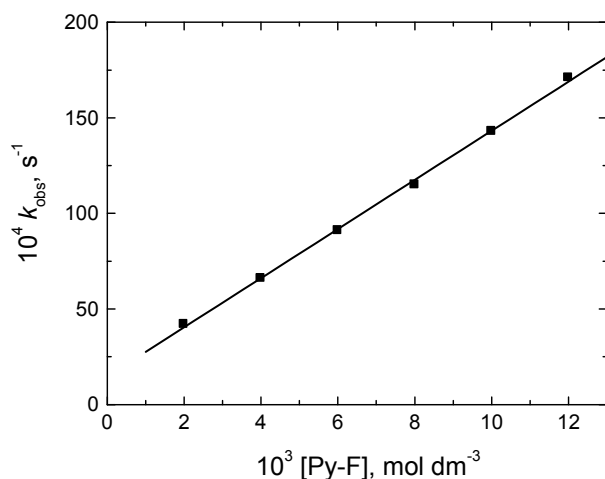**Figure 2.** *Plot of k_{obs} versus [Py-F] in the oxidation of Py-F by Ce(IV) in perchloric acid solution. [Ce(IV)] = 2.0 x 10^{-4}, [H^+] = 0.3 and I = 1.0 mol dm^{-3} at 20°C.*

Table 1. *Effect of [Ce(IV)], [Py-F] and [H^+] on k_{obs} in the oxidation of Py-F by Ce(IV) in perchloric acid solutions at 20°C.*

10^4 [Ce(IV)], mol dm^{-3}	10^3 [Py-F], mol dm^{-3}	[H^+], mol dm^{-3}	I, mol dm^{-3}	$10^4 k_{obs}$, s^{-1}
0.5	8.0	0.3	1.0	117
1.0	8.0	0.3	1.0	111
2.0	8.0	0.3	1.0	115
3.0	8.0	0.3	1.0	116
4.0	8.0	0.3	1.0	113
5.0	8.0	0.3	1.0	117
2.0	2.0	0.3	1.0	42
2.0	4.0	0.3	1.0	67
2.0	6.0	0.3	1.0	91
2.0	8.0	0.3	1.0	115
2.0	10.0	0.3	1.0	144
2.0	12.0	0.3	1.0	171
2.0	8.0	0.1	1.0	146
2.0	8.0	0.2	1.0	129
2.0	8.0	0.3	1.0	115
2.0	8.0	0.5	1.0	93
2.0	8.0	0.7	1.0	75
2.0	8.0	0.9	1.0	59
2.0	8.0	0.3	1.0	115
2.0	8.0	0.3	1.2	112
2.0	8.0	0.3	1.4	116
2.0	8.0	0.3	1.6	121
2.0	8.0	0.3	1.8	118
2.0	8.0	0.3	2.0	113

Experimental error ± 4%.

3.3. Effect of Ionic Strength and Dielectric Constant of the Reaction Medium

The effect of ionic strength on the rate of the reaction was studied by varying the ionic strength in the range 1.0 – 2.0 mol dm^{-3} using sodium perchlorate as an inert electrolyte with keeping the concentrations of all other reactants constant. The results indicated that variation of ionic strength was found to have negligible effect on the reaction rate.
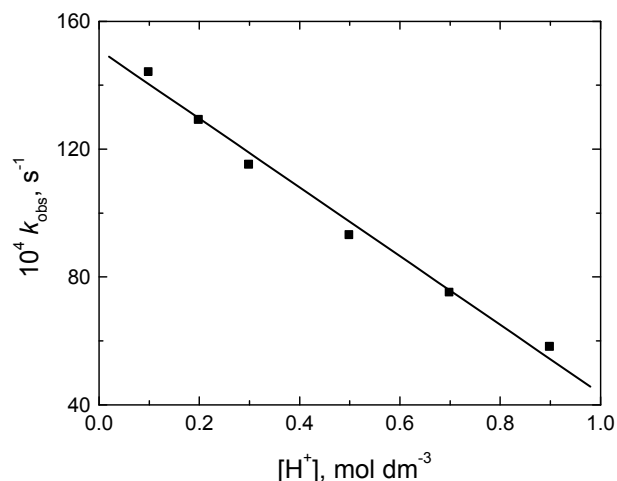

Figure 3. *Plot of k_{obs} versus [H^+] in the oxidation of Py-F by Ce(IV) in perchloric acid solution. [Py-F] = 8.0 x 10^{-3}, [Ce(IV)] = 2.0 x 10^{-4} and I = 1.0 mol dm^{-3} at 20°C.*

The dielectric constant (*D*) effect was studied by varying the acetic acid - water content in the reaction mixture with all other conditions being kept constant. The dielectric constant was computed from the values of dielectric constants of pure liquids by considering their *D* in pure form using equation: $D = D_1V_1 + D_2V_2$, where V_1 and V_2 are volume fractions and D_1 and D_2 are dielectric constants of water and acetic acid as 78.5 and 6.15, respectively. The rate constants increased negligibly with decreasing the dielectric constants of the reaction medium.

3.4. Effect of Initially Added Product

The effect of added cerium(III) product was studied in the concentration range 0.4 x 10^{-4} to 9.0 x 10^{-4} mol dm^{-3} at constant concentrations of the oxidant, reductant and acid. It was found that Ce(III) did not have any significant effect on the rate of reaction.

3.5. Effect of Temperature

The rate of reaction was carried out at five temperatures namely, 293, 298, 303, 308 and 313 K, at constant concentrations of the reactants and other conditions being constant. The results indicate that the observed first order rate constant was increased with raising temperature. The activation parameters of the second order rate constant (k_2) are calculated using Arrhenius, Figure 4a, and Eyring, Figure 4b, plots and are listed in Table 2.
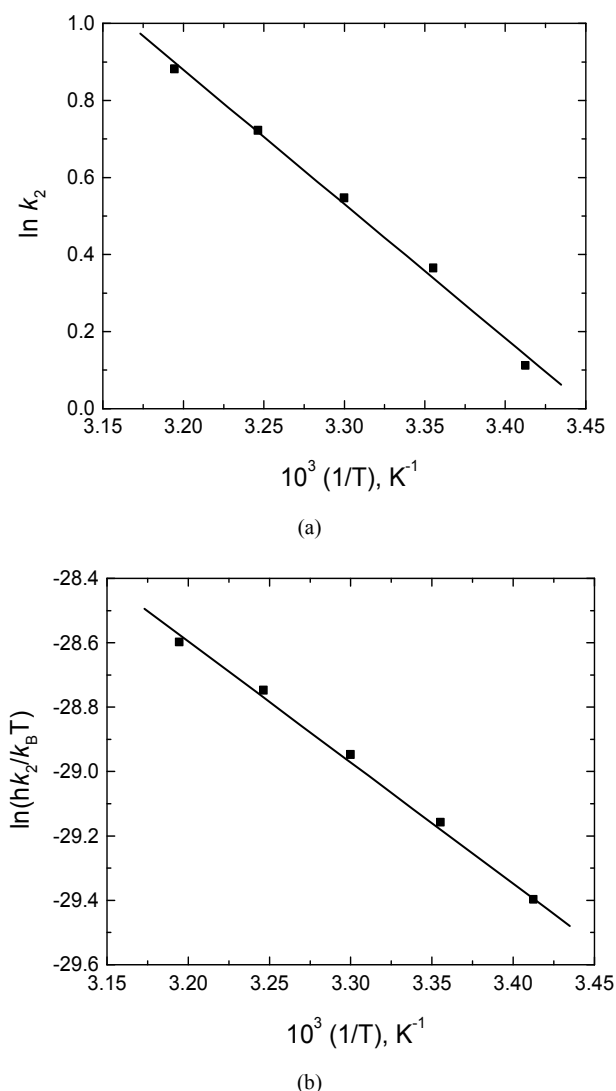
(a)

(b)

Figure 4. *a) Arrhenius and, b) Eyring plots in the oxidation of Py-F by Ce(IV) in perchloric acid solutions. [Py-F] = 8.0 x 10^{-3}, [Ce(IV)] = 2.0 x 10^{-4}, [H^+] = 0.3 and I = 1.0 mol dm^{-3}.*

Table 2. *Activation parameters of the second order rate constant k_2 in the oxidation of Py-F by Ce(IV) in perchloric acid solutions. [Py-F] = 8.0 x 10^{-3}, [Ce(IV)] = 2.0 x 10^{-4}, [H^+] = 0.3 and I = 1.0 mol dm^{-3}.*

$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta G^{\neq}_{298}$, kJ mol^{-1}	$E_a^{\neq}$, kJ mol^{-1}
-139.68	30.76	72.83	29.59

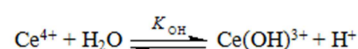Experimental error ± 4%.

3.6. Polymerization Test

The intervention of free radicals during the reaction was examined by polymerization test. The reaction mixture to which a known quantity of acrylonitrile scavenger has been added initially was kept in an inert atmosphere for about 6 h. Upon diluting the reaction mixture with methanol, a white precipitate has been formed, suggesting generation of a free radical in the reaction. When the experiment was repeated in the absence of Py-F under similar conditions, the test was negative. This indicates that the reaction was routed through a free radical path.
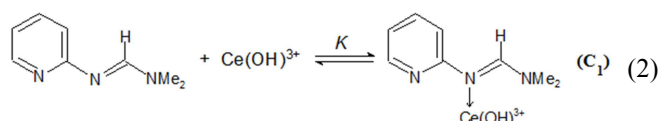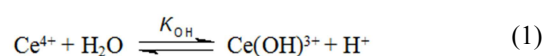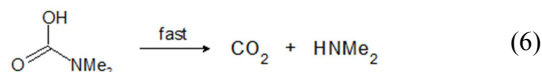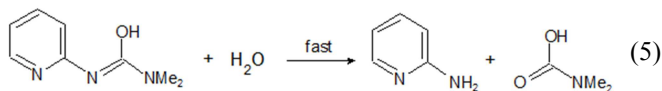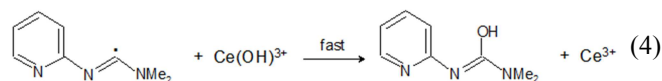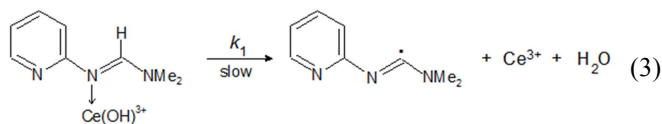
4. Discussion

It was reported [25-27] that the active species of cerium(IV) in perchloric acid solutions 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} up to the concentration of 1.5 x 10^{-3} mol dm^{-3} of cerium(IV), whereas the hydrolyzed forms and dimers are the more 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,

$$Ce^{4+} + H_2O \xrightleftharpoons{K_{OH}} Ce(OH)^{3+} + H^+$$

The present reaction between Py-F and Ce(IV) in aqueous perchloric acid solutions has a stoichiometry of 1: 2, i.e., one mole of Py-F requires two moles of Ce(IV). The reaction exhibited first order dependence with respect to [Ce(IV)], less than unit order with respect to [Py-F] and negative fractional order in $[H^+]$. The rate is not considerably affected by Ce(III) suggesting that the probability of any fast equilibrium with the product preceding the rate-determining step was ruled out. 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 radical as obtained experimentally. The rate of reaction was not considerably affected by variation of either ionic strength or dielectric constant of the reactions medium suggesting that the reaction occur between a neutral molecule and a charged ion [31, 32].

The less than unit order with respect to [Py-F] may be as a result of complex formation between the kinetically active Ce(IV) species and Py-F (C_1) prior to the rate-determining step. Complex formation was proved kinetically by the non-zero intercepts of the plot of $1/k_{obs}$ versus $1/$[Py-F] (Figure 5) 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 formed complex was slowly decomposed in the rate-determining step to give rise to the initial oxidation products as the substrate radical (Py-F·) and Ce(III). The substrate radical reacts with another Ce(IV) species in a subsequent fast step to yield an intermediate product, *N, N*-dimethyl-*N'*-(pyridin-2-yl) urea. In a further fast step, the intermediate product is hydrolyzed to give the final oxidation products as given in the following mechanistic scheme,

$$Ce^{4+} + H_2O \xrightleftharpoons{K_{OH}} Ce(OH)^{3+} + H^+ \qquad (1)$$

(2)

$$\text{(3)}$$

$$\text{(4)}$$

$$\text{(5)}$$

$$\text{(6)}$$

Since the mechanistic scheme 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 radical intermediate as was obtained experimentally.

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

$$\text{Rate} = \frac{k_1 K_{OH} K [\text{Ce(IV)}][\text{Py}-\text{F}]}{[\text{H}^+] + K_{OH} + K_{OH} K [\text{Py}-\text{F}]} \qquad (7)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (8),

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k_{obs}[\text{Ce(IV)}] \qquad (8)$$

Comparing Eqs. (7) and (8), the following relationship is obtained,

$$k_{obs} = \frac{k_1 K_{OH} K [\text{Py}-\text{F}]}{[\text{H}^+] + K_{OH} + K_{OH} K [\text{Py}-\text{F}]} \qquad (9)$$

The rate law (7) is consistent with all the observed orders with respect to different species, which can be verified by rearranging to the following equations,

$$\frac{1}{k_{obs}} = \left(\frac{[\text{H}^+] + K_{OH}}{k_1 K_{OH} K} \right) \frac{1}{[\text{Py}-\text{F}]} + \frac{1}{k_1} \qquad (10)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_{OH} K [\text{Py}-\text{F}]} \right)[\text{H}^+] + \frac{1}{k_1 K [\text{Py}-\text{F}]} + \frac{1}{k_1} \qquad (11)$$

According to Eqs. (10) and (11), plots of $1/k_{obs}$ versus $1/[\text{Py}-\text{F}]$ at constant $[\text{H}^+]$, and $1/k_{obs}$ versus $[\text{H}^+]$ at constant $[\text{Py}-\text{F}]$ should be linear with positive intercepts and are found to be so as shown in Figures 5 and 6, respectively. From the slopes and intercepts of these plots, the values of k_1, K_{OH}, and K could be evaluated and were found to be 31.25 x 10^{-3} s^{-1}, 0.17 mol dm^{-3}, and 202.17 dm^3 mol^{-1}, respectively at 20 °C.

The obtained activation parameters listed in Table 2 can be discussed as follows. The negative value of $\Delta S^{\#}$ suggests interaction of reacting ions to form an intermediate complex

of inner-sphere nature [34, 35]. This value is within the range of radical reactions and has 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 $\Delta H^{\#}$ and $\Delta S^{\#}$ are both favorable for electron transfer processes. On the other hand, the positive values of both $\Delta H^{\#}$ and $\Delta G^{\#}$ indicate endothermic formation of the complex and its non-spontaneity, respectively.
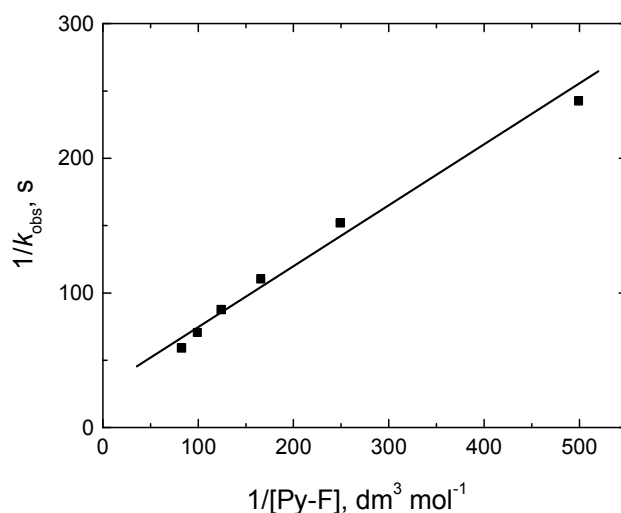

Figure 5. Plot of $1/k_{obs}$ versus $1/[Py\text{-}F]$ in the oxidation of Py-F by Ce(IV) in perchloric acid solution. [Ce(IV)] = 2.0 x 10^{-4}, [H$^+$] = 0.3 and I = 1.0 mol dm^{-3} at 20°C.

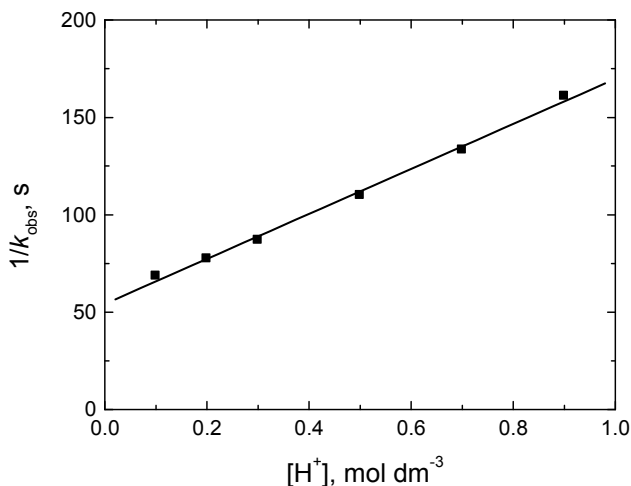**Figure 6.** Plot of $1/k_{obs}$ versus [H$^+$] in the oxidation of Py-F by Ce(IV) in perchloric acid solution. [Py-F] = 8.0 x 10^{-3}, [Ce(IV)] = 2.0 x 10^{-4} and I = 1.0 mol dm^{-3} at 20°C.

Appendix A. Derivation of the Rate Law Expression

According to the suggested mechanism and regarding to reaction (3),

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k_1[\text{C}_1] \qquad (A1)$$

Regarding to reactions (1) and (2),

$$K_{OH} = \frac{[Ce(OH)^{3+}][H^+]}{[Ce^{4+}]}, \qquad [Ce(OH)^{3+}] = \frac{K_{OH}[Ce^{4+}]}{[H^+]} \qquad (A2)$$

and

$$K = \frac{[C_1]}{[Ce(OH)^{3+}][Py\text{-}F]},$$

$$[C_1] = K[Ce(OH)^{3+}][Py\text{-}F] = \frac{K_{OH}K[Ce^{4+}][Py\text{-}F]}{[H^+]} \qquad (A3)$$

Substituting Eq. (A3) into Eq. (A1) leads to,

$$Rate = \frac{k_1 K_{OH} K[Ce^{4+}][Py\text{-}F]}{[H^+]} \qquad (A4)$$

The total concentration of Py-F is given by:

$$[Py\text{-}F]_T = [Py\text{-}F]_F + [C_1] \qquad (A5)$$

where 'T' and 'F' stand for total and free concentrations.
Substituting Eq. (A3) into Eq. (A5) and rearrangement gives,

$$[Py\text{-}F]_T = [Py\text{-}F]_F + \frac{K_{OH}K[Ce^{4+}][Py\text{-}F]}{[H^+]} \qquad (A6)$$

$$[Py\text{-}F]_T = [Py\text{-}F]_F(1 + \frac{K_{OH}K[Ce^{4+}]}{[H^+]}) \qquad (A7)$$

Therefore,

$$[Py\text{-}F]_F = \frac{[Py\text{-}F]}{1 + \frac{K_{OH}K[Ce^{4+}]}{[H^+]}} \qquad (A8)$$

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

$$[Py\text{-}F]_F = [Py\text{-}F]_T \qquad (A9)$$

Also,

$$[Ce(IV)]_T = [Ce^{4+}]_F + [Ce(OH)^{3+}] + [C_1] \qquad (A10)$$

Substituting Eqs. (A2) and (A3) into Eq. (A10),

$$[Ce(IV)]_T = [Ce^{4+}]_F + \frac{K_{OH}[Ce^{4+}]}{[H^+]} + \frac{K_{OH}K[Ce^{4+}][Py\text{-}F]}{[H^+]} \qquad (A11)$$

$$[Ce(IV)]_T = [Ce^{4+}]_F (1 + \frac{K_{OH}}{[H^+]} + \frac{K_{OH}K[Py\text{-}F]}{[H^+]}) \qquad (A12)$$

$$[Ce^{4+}]_F = \frac{[Ce(IV)]_T}{1 + \frac{K_{OH}}{[H^+]} + \frac{K_{OH}K[Py\text{-}F]}{[H^+]}} \qquad (A13)$$

Substituting Eqs. (A9) and (A13) into Eq. (A4) (and omitting 'T' and 'F' subscripts) leads to,

$$Rate = \frac{k_1 K_{OH} K[Ce(IV)][Py\text{-}F]}{1 + \frac{K_{OH}}{[H^+]} + \frac{K_{OH}K[Py\text{-}F]}{[H^+]}} = \frac{k_1 K_{OH} K[Ce(IV)][Py\text{-}F]}{[H^+] + K_{OH} + K_{OH}K[Py\text{-}F]} \qquad (A14)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (A15),

$$Rate = \frac{-d[Ce(IV)]}{dt} = k_{obs}[Ce(IV)] \qquad (A15)$$

Comparing Eqs. (A14) and (A15), the following relationship is obtained,

$$k_{obs} = \frac{k_1 K_{OH} K[Py\text{-}F]}{[H^+] + K_{OH} + K_{OH}K[Py\text{-}F]} \qquad (A16)$$

and with rearrangement, the following equations are obtained,

$$\frac{1}{k_{obs}} = \left(\frac{[H^+] + K_{OH}}{k_1 K_{OH} K_1}\right)\frac{1}{[Py\text{-}F]} + \frac{1}{k_1} \qquad (A17)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_{OH} K_1[Py\text{-}F]}\right)[H^+] + \frac{1}{k_1 K_1[Py\text{-}F]} + \frac{1}{k_1} \qquad (A18)$$

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