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PICOLINIC ACID PROMOTED OXIDATIVE DECARBOXYLATION OF PHENYLSULFINYLACETIC ACID BY Cr(VI)

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ABSTRACT. The kinetics and mechanism of picolinic acid promoted reaction of phenylsulfinylacetic acid (PSAA) with Cr(VI) was carried out in aqueous acetonitrile medium under pseudo first order conditions. The reaction follows Michaelis-Menten type of kinetics with respect to PSAA. The catalytic activity by picolinic acid can be interpreted on the basis of the formation of a highly active oxidizing species, Cr(VI)-PA complex. The mechanism involves the formation of a termolecular complex, Cr(VI)-PA-PSAA by the nucleophilic attack of the sulfur atom of PSAA on chromium of Cr(VI)-PA complex in an equilibrium step followed by ligand coupling in a slow step. Electron releasing substituents in the phenyl ring of PSAA accelerate while electron withdrawing groups retard the reaction rate. The overall rate constants for the para- and meta-substituted PSAAs are found to correlate excellently with Hammett σ constants with a very low reaction constant, ρ.

KEY WORDS: Phenylsulfinylacetic acid, Cr(VI), Picolinic acid, Oxidative decarboxylation, Substituent effect, Catalysis

INTRODUCTION

Cr(VI) is an excellent oxidizing agent for both preparative and analytical purposes. During oxidation reactions, the main co-ordination site of Cr binding involves alcoholato, carboxylato and thiolato groups [1, 2]. The pyridine bases and other ligands containing hetero nitrogen atoms were found to facilitate the Cr(VI) oxidation reactions to a greater extent and the various chelating agents explored for this purpose are picolinic acid, pyridine-2,6-dicarboxylic acid, 2,2'-bipyridyl, 1,10-phenanthroline, EDTA, etc. In the presence of chelating agents the redox activity of Cr(VI) has been found to change drastically. The complexing agents influence the nature of Cr(VI) species in the reaction mixture and even affect the mechanism of Cr(VI) oxidation in some cases.

Picolinic acid (PA), an endogenous metabolite of L-tryptophan that has been detected in a variety of biological media including cell culture supernatants, blood serum [3], cerebrospinal fluid [4], pancreatic juice and intestinal homogenates [5], possesses a wide range of neuroprotective, immunological and anti-proliferative effects [6]. PA is an efficient chelating agent which forms mono and bis complexes through pyridine nitrogen and carboxylate oxygen [7] with a range of metals including Tl, Mo and W [8, 9]. Capitalizing on its chelation properties, PA-metal complexes are widely used as means of introducing bioactive metals into biological systems [10, 11]. In the case of PA catalyzed Cr(VI) oxidation reactions, PA is not itself oxidized but lost during the reaction due to the formation of an inert Cr(III)-PA complex. Thus PA is not a true catalyst and it is better described as a promoter. Picolinic acid promoted Cr(VI) oxidation of several organic substrates [12-16] including organic sulfur compounds [12, 17-19] have been extensively studied. The catalytic effect was attributed to the activation of oxidizing species of chromium through a precursor complex formation.

Though phenylsulfinylacetic acid (PSAA) is a versatile compound finding utility in pharmaceutical and synthetic fields [20-26], literature survey clearly reveals that there is no

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systematic mechanistic study on the oxidation of PSAA except our recent publications [27-31]. Hence, in continuation of our work it is decided to carry out a systematic investigation on the PA promoted Cr(VI) reaction with PSAA with a view to proposing a suitable mechanistic path.

EXPERIMENTAL

Phenylsulfinylacetic acid and several para- and meta-substituted PSAAs were synthesized from the corresponding phenylthioacetic acids via controlled oxidation using equimolar amount of H_2O_2 [32] and recrystallised from suitable solvents [33]. The purity of the samples was checked by LCMS and comparing their melting points with the literature values [33]. Potassium dichromate (Merck), sodium perchlorate (Merck), $HClO_4$ (Merck) and picolinic acid (SDS) were of AnalaR grade and were used as received. The solvents, acetonitrile and water were purified by literature methods.

Kinetic measurements

The kinetic measurements were performed by monitoring absorbance changes using Elico Double beam UV-vis Bio-spectrophotometer with an inbuilt thermostat, under pseudo first order conditions by maintaining [PSAA] » [Cr(VI)] in 40% acetonitrile - 60% water (v/v) medium in the presence of PA. The disappearance of Cr(VI) was followed at 351 nm until 75% of Cr(VI) was consumed and the spectral changes observed at different time intervals during the reaction are given in Figure 1. Sodium perchlorate and perchloric acid were used to maintain the ionic strength and acidity of the medium, respectively.

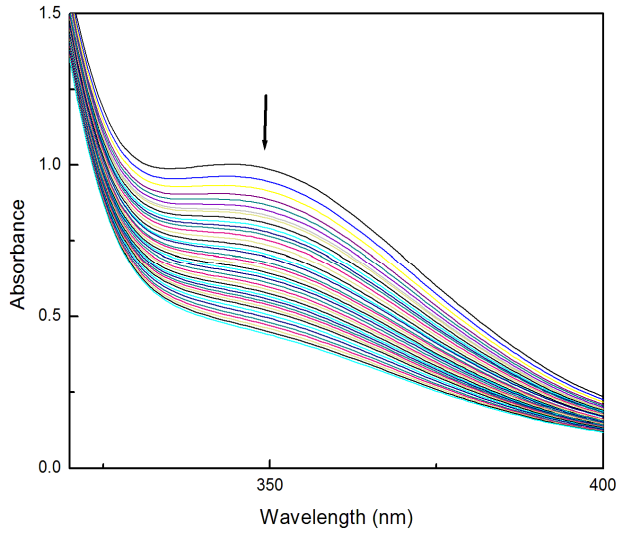


Figure 1. UV-visible spectra for the kinetic run. [PSAA] = 5.0 x 10^{-2} mol dm^{-3}; [Cr(VI)] = 5.0 x 10^{-4} mol dm^{-3}; [PA] = 0.3 mol dm^{-3}; [H^+] = 0.75 mol dm^{-3}.

The pseudo-first order rate constant (k_1) for each kinetic run was evaluated from the slope of log OD vs time by the method of least squares. The precision of k values is given in terms of 95% confidence limits of Student's t test.

Product analysis

The reaction mixture with excess of [Cr(VI)] over [PSAA] was kept for 48 hours to ensure completion of the reaction and the solution was then extracted with ether. The ether layer was collected, dried over anhydrous sodium sulfate and the solvent was removed by evaporation. The GC-MS chromatogram of the product (Figure 2) with 100% abundance eluted at a retention time of 12.47 AV gave the base parent peak at m/z = 156. The value shows the molar mass of methyl phenyl sulfone. The peak position and fragmentation pattern exactly matches with that of the reference, methyl phenyl sulfone (Figure 2 - inset). This is further confirmed by IR spectroscopy (Figure 3) which shows strong bands at 1148 cm^{-1} and 1290 cm^{-1} characteristic of symmetric and asymmetric stretching respectively of $>SO_2$ group [34, 35]. The other characteristic absorption frequencies (cm^{-1}) of methyl phenyl sulfone are sp^2 C-H stretch (3024), sp^2 C-H bend (744), sp^3 C-H stretch (2922), sp^3 C-H bend (1451), aromatic C=C (1647) and aromatic C-C stretch (1402).

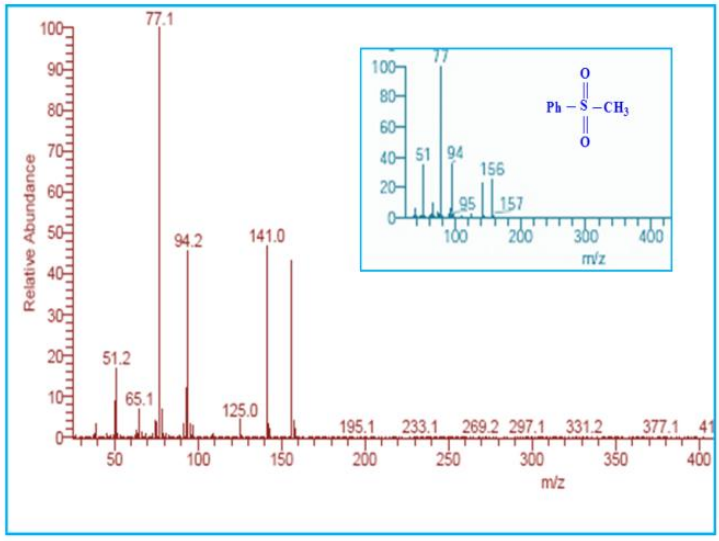


Figure 2. GC-MS spectrogram of the product.

The UV-visible spectroscopy aids in the determination of the final fate of Cr(VI) in the reaction mixture. The UV-visible spectra of Cr(III) ion shows two peaks at 421 nm and 592 nm which are attributed to the octahedral transitions, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ [36-38] whereas the spectrum of the product mixture exhibits two peaks at 408 nm and 542 nm (Figure 4). This clearly demonstrates that Cr(VI) is reduced to Cr(III) ion but the blue shift observed in λ_{max} values for the product mixture is due to existence of Cr(III) in the form of complex, probably the Cr(III)-PA complex as reported in the PA catalysed Cr(VI) oxidation reactions [12-14].

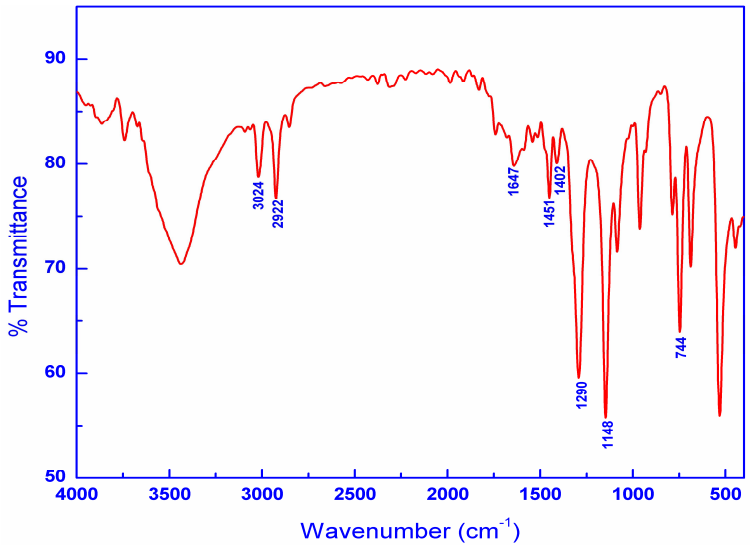


Figure 3. IR spectrum of the product.

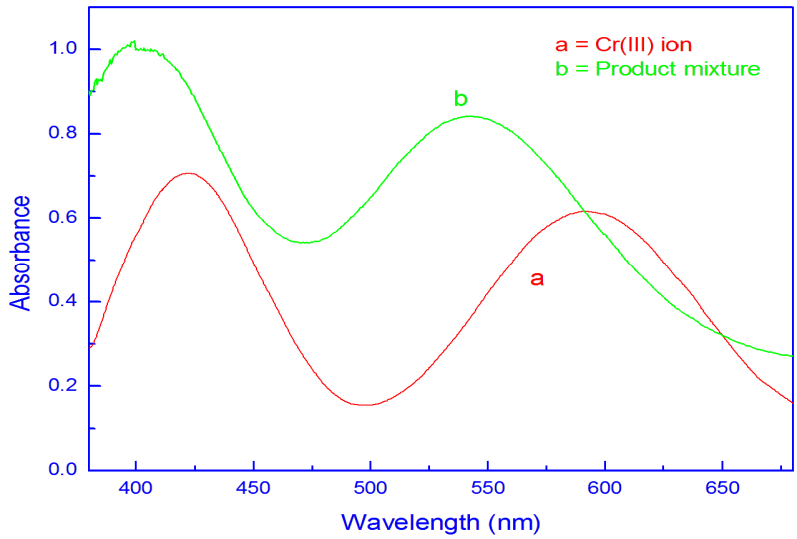


Figure 4. UV-visible spectra of Cr(III) ion and product mixture.

RESULTS

That the reaction exhibits first order dependence on Cr(VI) in the presence of PA is obvious from the linear log OD vs time plots even upto 75% completion of the reaction and from constant k_1 values obtained at different initial [Cr(VI)] (Table 1). The second order rate constants obtained using the relation $k_2 = k_1/[PSAA]$ are not found to be constant. Further, the

double logarithmic plot of k_1 vs [PSAA] is linear (r = 0.999) with slope = 0.61 ± 0.01 indicating that the reaction is of fractional order (0.61) with respect to PSAA. Hence, the overall rate of the reaction, k_{ov} is obtained from the relation, $k_{ov} = k_1 / [PSAA]^{0.61}$. The plot of k_1^{-1} vs $[PSAA]^{-1}$ is linear (r = 0.998) with an intercept on the rate axis indicating the Michaelis-Menten dependence on PSAA [39].

Table 1. Pseudo-first order and overall rate constants for the reaction.

10^2[PSAA] (mol dm^{-3})	10^4[Cr(VI)] (mol dm^{-3})	$10^4 k_1$ (s^{-1})	$10^3 k_{ov}$ ($dm^3 mol^{-1})^{0.61} s^{-1}$
1.0	5.0	3.70 ± 0.13	6.15± 0.13
3.0	5.0	7.65 ± 0.07	6.49± 0.02
5.0	5.0	10.0± 0.11	6.22± 0.02
7.0	5.0	12.3 ± 0.02	6.21± 0.01
10	5.0	15.3 ± 0.05	6.23± 0.01
5.0	1.0	9.30 ± 0.46	5.78± 0.09
5.0	3.0	9.96 ± 0.03	6.19± 0.01
5.0	7.0	9.54 ± 0.39	5.93± 0.08

[PA] = 0.3 mol dm^{-3}; [H^+] = 0.75 mol dm^{-3}; I = 0.80 mol dm^{-3}; solvent = 40% acetonitrile - 60% water (v/v) ; T = 30 °C.

The reaction is greatly influenced by the acidity of the medium (Table 2) and the order in [H^+] is unity which is evident from the linear log-log plot of k_1 against [H^+] (r = 0.999) with slope = 1.0 ± 0.02. The rate increases significantly with increasing acetonitrile content of the medium (Table 2) suggesting a facile reactivity in a medium of low dielectric constant.

The effect of picolinic acid on the reaction rate indicates a slight increase in rate with increase in the concentration of PA initially up to 0.15 mol dm^{-3} and after that an appreciable linear enhancement of rate is noted with increase in [PA]. The effect of PA is depicted in Table 2. The double inverse plot of k_1 vs [PA] in the 0.15-0.5 mol dm^{-3} range shows an intercept in the rate axis which confirms the reversible complex formation of PA with any one of the reactants.

Table 2. Effect of [H^+], [PA], solvent composition and temperature on rate.

10^2 PA (mol dm^{-3})	$10^4 k_1$ [a] (s^{-1})	10^1[H^+] (mol dm^{-3})	$10^4 k_1$ [b] (s^{-1})	CH_3CN-H_2O (%,v/v)	$10^4 k_1$ [c] (s^{-1})	T (ºC)	$10^3 k_{ov}$ [d] ($dm^3 mol^{-1})^{0.61} s^{-1}$
0	6.49 ± 0.25	3.0	4.10 ± 0.13	20 - 40	8.23 ± 0.12	20	2.75 ± 0.09
0.50	6.94 ± 0.10	5.0	6.98 ± 0.12	40 - 60	10.0 ± 0.11	25	4.12 ± 0.01
5.0	7.92 ± 0.11	7.5	10.2 ± 0.09	60 - 80	12.7 ± 0.08	30	6.22 ± 0.12
8.0	7.93 ± 0.11	9.0	12.3 ± 0.05	80 - 20	16.1 ± 0.11	35	8.23 ± 0.17
15	7.93 ± 0.03	10	14.0 ± 0.52				
25	9.97 ± 0.06						
30	10.0 ± 0.11						
40	12.1 ± 0.04						
50	13.8 ± 0.06						

[PSAA] = 5.0 x 10^{-2} mol dm^{-3}; [Cr(VI)] = 5.0 x 10^{-4} mol dm^{-3}; [H^+] = 0.75 mol dm^{-3}; CH_3CN-H_2O (40-60% , v/v); [a,c,d]I = 0.8 mol dm^{-3} ; [b]I = 1.1 mol dm^{-3}.

The reaction is carried out at four different temperatures viz., 20, 25, 30 and 35 ºC and the k_{ov} values are presented in Table 2. The thermodynamic parameters are evaluated from the intercept and slope of the Eyring plot of log k_{ov}/T vs 1/T. The entropy of activation, $\Delta S^{\neq}$ and enthalpy of activation, $\Delta H^{\neq}$ calculated for the PA promoted Cr(VI) reaction of PSAA are -112.38 ± 6.6 J K^{-1} mol^{-1} and 53.17 ± 1.9 KJ mol^{-1} respectively whereas for the uncatalysed reaction the values are -24.49 ± 0.09 J K^{-1} mol^{-1} and 75.58 ± 2.5 KJ mol^{-1} respectively which follow the trend expected for the catalysed reaction.

As the study of substituent effect gives positive evidences on the nature of transition state and mechanism, the effect of substituents on the PA catalysed oxidative decarboxylation rate is carried out with several para- and meta- substituted phenylsulfinylacetic acids at 30 ºC. The plot of log k_{ov} vs Hammett constants, σ gives an excellent correlation (Figure 5, r = 0.997) with low negative reaction constant, ρ (ρ = -0.322 ± 0.01).

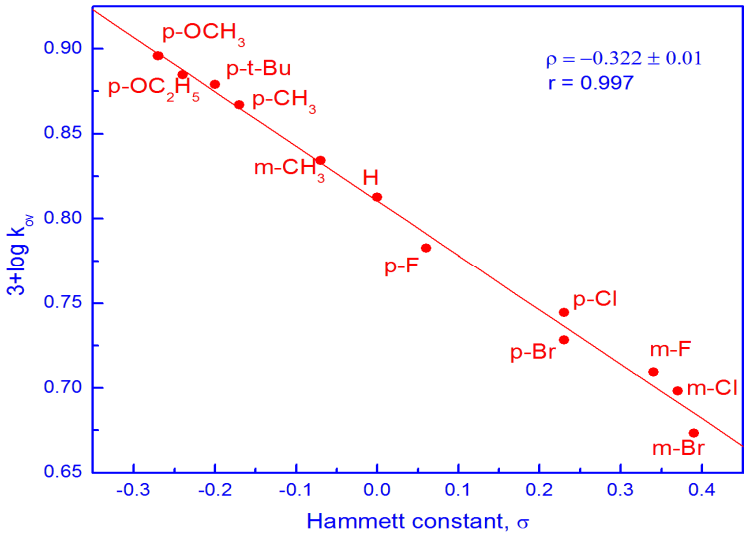
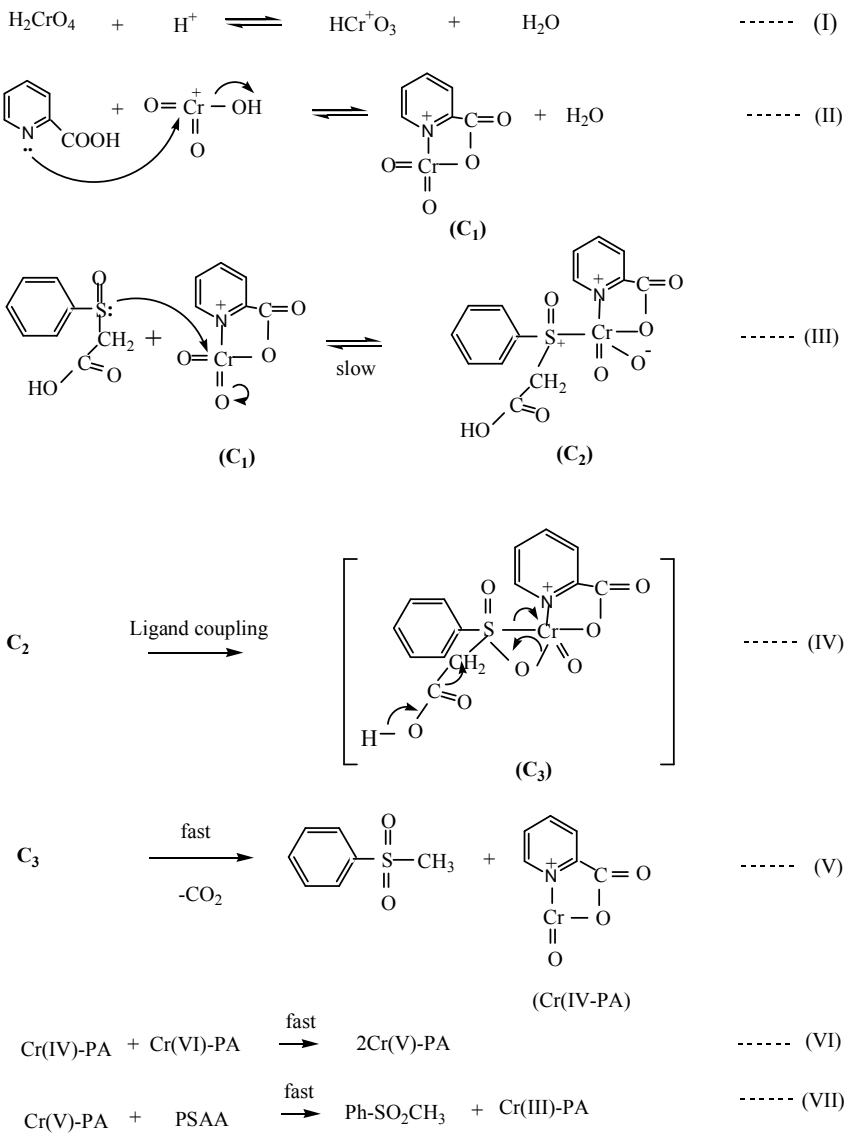


Figure 5. Hammett plot at 30 ºC.

DISCUSSION

The active oxidizing species involved in the reaction may be Cr(VI) itself or Cr(V) formed as a result of one-electron transfer or Cr(IV) due to two-electron transfer. The absence of absorption at 750 nm, where Cr(V) is the only absorbing species [40], rules out the involvement of Cr(V) as an active species. Besides, the insensitivity of rate to added radical scavenger, acrylamide, clearly rules out the single-electron transfer mechanism and hence the involvement of Cr(V) species in the reaction mechanism. The added Mn^{2+} ion, scavenger for Cr(IV), has failed to produce any noticeable effect on the reaction rate ruling out the participation of Cr(IV) as the active species. Thus, the active species in this reaction is Cr(VI) itself, which exists in aqueous acidic solution in a variety of forms such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ besides other protonated forms like $HCrO_3^+$, H_2CrO_4, $H_2Cr_2O_7$ and $HCr_2O_7^-$ depending on [Cr(VI)] and the pH of the medium [41-44]. If the concentration is above 0.05 mol dm^{-3}, Cr(VI) mainly exists as dimeric forms while at lower concentrations it exists predominantly in monomeric forms [41, 45, 46]. At lower concentrations of H^+, $HCrO_4^-$ is the main species whereas $HCrO_3^+$ is the major moiety at higher [H^+] [45, 47, 48]. Thus, under the present experimental conditions of high [H^+] and low [Cr(VI)], $HCrO_3^+$ species is assumed to be the active form of Cr(VI). The first order dependence of the reaction rate on [H^+] and [Cr(VI)] are in agreement with the existence of $HCrO_3^+$ species.

In earlier reports [12, 14, 49] it has been observed that the redox potential of Cr(VI) increases in the presence of chelating agents and believed that Cr(VI) forms complexes with the chelating agents. Thus in the present case, the increase in reaction rate with increase in [PA] may be attributed to the formation of a bimolecular cyclic complex (C_1, Scheme 1) between Cr(VI) and PA which is assumed to be the kinetically active oxidizing species [12, 17-19].



Scheme 1

The spectral evidence for the formation of Cr(VI)-PA complex is obtained from the hyperchromic shift and broadening of the UV absorption peak at 263 nm after the addition of PA to Cr(VI) (Figure 6).

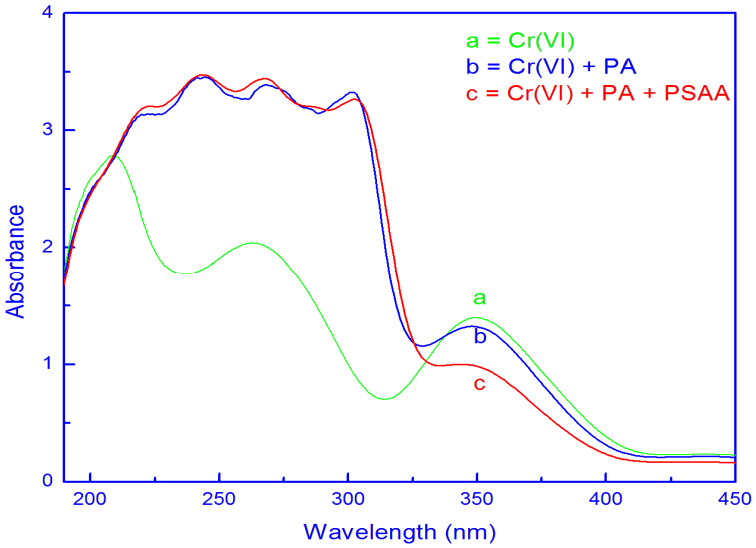


Figure 6. UV-vis absorption spectra. [PSAA] = 5.0 x 10^{-2} mol dm^{-3}; [Cr(VI)] = 5.0 x 10^{-4} mol dm^{-3}; [PA] = 0.3 mol dm^{-3}; [H^+] = 0.75 mol dm^{-3}.

The high reactivity in the presence of PA, confirms that the cationic Cr(VI)-PA complex (C_1) is a more efficient electrophile than $HCrO_3^+$ itself. The involvement of positive active species in the reaction is proved from the study of dielectric constant of the medium, i.e. a positive slope is obtained when log k_1 is plotted against 1/dielectric constant of the medium. The appreciably high value of Michaelis constant, K_m = 0.204 mol dm^{-3}, obtained from the plot of $1/k_1$ vs 1/[PA] in the range 0.15-0.5 mol dm^{-3} illustrate that only weak binding exists between PA and Cr(VI) during the formation of Cr(VI)-PA complex.

The chromium atom of Cr(VI)-PA complex, C_1 then receives a nucleophilic attack by the sulfur atom of PSAA to form a termolecular complex, C_2 in a slow step. As the reaction has a non-integral kinetic order for PSAA it is reasonable to envisage that the reaction follows Michaelis-Menten kinetics:

$$1/k_1 = 1/k + K_m/k[PSAA]$$

By applying Michaelis-Menten kinetics, the values of k and K_m were evaluated from the slope and intercept of the double inverse plot of k_1 against [PSAA]. The values of k and K_m obtained are 2.04 x 10^{-3} s^{-1} and 4.54 x 10^{-2} mol dm^{-3}. The nature of binding of PSAA with the active species is found to be moderately high as inferred from the low K_m value. The spectral evidence for the formation of termolecular complex is obtained from the noticeable hypochromic shift at 351 nm (Figure 7c) in the UV-visible spectrum of the reaction mixture containing PSAA.

As a result of nucleophilic attack of PSAA on C_1, a positive charge is developed on the sulfur atom of PSAA in the intermediate complex C_2. The trend of the reaction with different substituents indicates that the electron releasing substituents in the para- and meta- positions accelerate the reaction whereas electron withdrawing groups retard the reaction rate. This can be explained on the basis of stabilization of the positive sulfur centre in complex C_2 by electron releasing substituents and destabilization by electron withdrawing substituents.

The ternary complex then undergoes ligand coupling in a subsequent step to form the intermediate, C_3. The observed low negative reaction constant, ρ may be visualized due to the neutralization of positive charge on sulfur atom as a result of ligand coupling with oxygen atom. Such a ligand coupling pathway has already been suggested by the researchers in the PA catalysed Cr(VI) oxidation of organic sulfur compounds [12, 50]. The intermediate, C_3 then cleaves at α-β position to eliminate CO_2 followed by oxygen atom transfer to sulfur in fast steps leading to the formation of the product, methylphenyl sulfone. Thus, Cr(IV)-PA species is formed as a result of two electron transfer which participates in the faster steps with Cr(VI) to give Cr(V) [51] and consequently, Cr(V) oxidizes another PSAA molecule and itself gets reduced to Cr(III)-PA species. The Cr(V)-Cr(III) couple has a potential of 1.75 V, which would enable the rapid conversion of Cr(V) to Cr(III) after the reaction with the substrate [52].

CONCLUSION

The observed spectral changes in the picolinic acid promoted reaction of phenylsulfinylacetic acid (PSAA) with Cr(VI) in aqueous acetonitrile media evidence the formation of Cr(VI)-PA complex and the termolecular complex formed between Cr(VI), PA and PSAA. The reaction follows Michaelis-Menten kinetics with respect to PSAA. The ternary complex then undergoes ligand coupling followed by several fast steps to form the products. The trend of the reaction with different meta- and para-substituted PSAAs indicates that the electron releasing substituents accelerate the reaction whereas electron withdrawing groups retard the reaction rate.

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