

## Oxidation of *S*-Phenylmercaptoacetic Acid by Piperidinium Chlorochromate<sup>†</sup>

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**Abstract:** Oxidation of *S*-phenylmercaptoacetic acid by piperidiniumchlorochromate (PipCC) in the presence of perchloric acid has been studied in 50% (v/v) aqueous acetic acid medium. The reaction shows unit order dependence each with respect to oxidant and substrate. The order with respect to hydrogen ion concentration is fractional. The rate of oxidation increases with increase in the percentage of acetic acid and increase the ionic strength has negligible effect on the reaction rate. Number of electron transferred during the oxidation process has also determined. From the kinetic observations, the reaction mechanism and rate law has been proposed.

**Keywords:** Kinetics, Oxidation, Parameters, Piperidinium chlorochromate

### Introduction

A large number of chromium(VI) complexes are being used in the oxidation of organic compounds especially in the construction of natural structures, synthesis of hormones, prostaglandin and their synthones. Piperidinium chlorochromate (PipCC) has been used as a mild, efficient and selective oxidizing reagent in synthetic organic chemistry<sup>1</sup>.

However, there are not many reports on the mechanistic aspects of reactions of PipCC. The kinetics of oxidation of *S*-phenylmercaptoacetic acid<sup>2-7</sup> by various oxidants has been reported. Herein, we report the results obtained from a detailed kinetic study on the oxidation of several substituted *S*-phenylmercaptoacetic acids with piperidinium chlorochromate.

### Experimental

*S*-phenyl mercapto acetic acid were prepared and purified by literature method<sup>8</sup>. Piperidinium chlorochromate was prepared by a known procedure<sup>1</sup> and its purity was checked by determining Cr(VI) concentration iodometrically. Acetic acid was refluxed over chromium trioxide for 6 h and then fractionated<sup>9</sup>. All other chemicals used were of AnalaR grade. Only double distilled water used throughout the experiment. The reaction mixture was homogeneous throughout the course of the reaction.

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### Kinetic measurements

The kinetic runs were followed by spectrophotometrically by using UV-Visible spectrophotometer at 470 nm. The temperature of the reaction mixture was maintained at the desired value to an accuracy of  $\pm 0.1$  °C by circulating thermostated water in the reaction vessel. The pseudo-first order rate constants were calculated from the slope of log absorbance versus time plots ( $r > 0.990$ ) and the results were reproducible to an accuracy of  $\pm 3$  %.

### Product analysis

The kinetic reaction mixture was left to stand for overnight with stirring and then extracted with ether. The extract was dried over anhydrous sodium sulphate and the solvent evaporated. The residue was subjected to TLC analysis on a silica gel plate developed in a solvent system of n-butanol - acetic acid - water (40 - 10 - 50 %). The IR spectra gives the following frequencies corresponding to the sulfoxide were observed.  $1024\text{ cm}^{-1}$  (= S = O group),  $1713\text{ cm}^{-1}$  (= C = O group) and  $3434\text{ cm}^{-1}$  (- COOH group).

## Results and Discussion

The reaction was studied under different experimental conditions in the presence of perchloric acid as catalyst in acetic acid - water medium. The reaction was found to be first order with respect to oxidant as evidenced by a good linearity in the plot of log absorbance versus time ( $r = 0.990$ ).

At constant concentration of the oxidant, perchloric acid and constant temperature, the rate of reaction increased steadily upon increasing the concentration of the substrate in Table 1. A linear plot of  $\log k$  versus  $\log [\text{Substrate}]$  with a slope of unity. It is clear that indication of the fact, the reaction has unit order dependence on the concentration of substrate.

The effect of acidity was studied by varying the concentration of perchloric acid and rate constants were found to increase with increase the concentration of perchloric acid (Table 1). But, the plot of  $\log k$  versus  $\log [\text{H}^+]$  was found to be linear with a fractional slope indicating fractional order dependence with respect to hydrogen ion concentration.

Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of ion and neutral molecule in the rate determining step. The acetic acid composition in the solvent mixture was varied while maintaining the other variables constant as shown in Table 1. The rate was found to increase considerably upon increasing the acetic acid content of the medium. This result is due to the fact that the reaction is facilitated by an increase in polarity or nucleophilicity.

**Table 1.** Rate data on the oxidation *S*-phenyl mercaptoaceticacid by piperidinium chlorochromate at 313 K

[PipCC] $10^3$ , mol dm <sup>-3</sup>	[PMAA] $10^3$ , mol dm <sup>-3</sup>	[H <sup>+</sup> ] $10$ , mol dm <sup>-3</sup>	[NaClO <sub>4</sub> ] $10^2$ , mol dm <sup>-3</sup>	% AcOH- H <sub>2</sub> O, v/v	[MnSO <sub>4</sub> ] $10^2$ , mol dm <sup>-3</sup>	$k_1$ $10^4$ , s <sup>-1</sup>
3.30 - 7.70	7.50	0.68	-	50:50	-	9.11 - 9.24
4.40	5.00 - 17.50	0.68	-	50:50	-	6.34 - 19.91
4.40	7.50	0.68 - 3.41	-	50:50	-	7.43 - 15.98
4.40	7.50	0.68	0.00-20.04	50:50	-	9.05 - 9.06
4.40	7.50	0.68	-	55:45-30:70	-	6.82-16.61
4.40	7.50	0.68	-	50:50	0.00-20.04	9.05-6.41

The addition of acrylonitrile, which is a good trapper of free radicals, did not have any retarding effect on the reaction. It indicates that no free radicals participation in the reaction. The rate of the reaction decreases with increase in the concentration of manganous sulphate<sup>10</sup>. Thus, it is possible that the reaction involves a two electron transfer process which is given in Table 1.

The rate constants were measured at four different temperatures viz., 303, 313, 323 and 333 K while maintaining the concentration of the substrate, oxidant and  $[H^+]$  constant. From the Eyring's plot<sup>11</sup> of  $\log k_2/T$  versus  $1/T$ , the thermodynamic and activation parameters were calculated in Table 2.

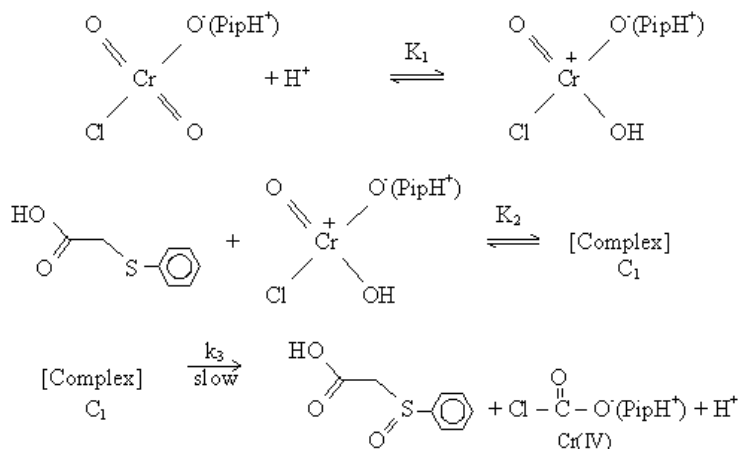
**Table 2.** Effect of temperature

Temperature, K	$k_1 \cdot 10^4, s^{-1}$
303	7.92
313	9.05
323	10.62
333	12.96

$$\Delta H^\ddagger = 4.78 \text{ kJmol}^{-1}, \Delta S^\ddagger = -184.57 \text{ JK}^{-1}\text{mol}^{-1}, \Delta G^\ddagger = 62.55 \text{ kJmol}^{-1}, E_a = 7.38 \text{ kJmol}^{-1}$$

### Mechanism and rate law

The reaction shows first order with respect to substrate, oxidant and fractional order with respect to  $[H^+]$ . The retardation of the rate by the addition of  $MnSO_4$  confirms that a two electron transfer process is involved in the reaction. Product analysis clearly indicates that the product was the corresponding sulfoxides. From these observations, the following mechanism and rate law are proposed.



**Scheme 1**

Rate law:

$$\begin{aligned}
 \text{Rate} &= k_3 [\text{Product}] \\
 &= k_3 K_2 [C_1] [S] \\
 \frac{-d[\text{PipCC}]}{dt} &= \frac{k_3 K_2 K_1 [S] [O] [H^+]}{1 + K_1 [H^+]} \\
 k_{\text{obs}} &= \frac{k_3 K_2 K_1 [S] [H^+]}{1 + K_1 [H^+]}
 \end{aligned}$$

The proposed mechanism and the suitable rate law support all the observations made including the effect of solvent polarity and the negative entropy of activation.

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