Duality on the oxidation of (phenylthio)acetic acids by vanadium (V) and iron (III)

K. Karunakaran, R. Gunumurthy
Department of Chemistry, Annamalai University, Annamalainagar 608 002, India.
and
K.P. Elango
Department of Chemistry, Gandhigram Rural Institute, Gandhigram 624 302, India.
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The kinetics of oxidation of (phenylthio)acetic acid and few para-substituted (phenylthio)acetic acids by vanadium(V) and iron(III) have been studied in acid medium. In both the cases, the order in substrate and oxidant is one each. Both the reactions are catalysed by hydrogen ions and follow a free radical path. A high negative $p$ value (-3.64) is obtained in the case of vanadium(V) oxidation and the product is the corresponding diphenyldisulphide. The $p$ value obtained in the iron(III) oxidation is -1.22 and the identified product is its sulphoxide. On the basis of the kinetic results suitable mechanisms have been proposed and discussed.

Much attention has been paid recently to the oxidation of organic sulphur compounds\(^1\)\(^-\)\(^9\). The mechanism and the products of these oxidations is largely dependent on the nature of the oxidants. First type of mechanism involves two equivalent oxidant resulting in the formation of sulphoxide as end product\(^1\)\(^-\)\(^7\). In the second type of mechanism one equivalent oxidant converts sulphides to disulphides\(^8\)\(^-\)\(^9\). Our earlier experiments on cerium (IV) (one electron transfer oxidant) oxidation of (phenylthio) acetic acid yielded diphenyldisulphide as the major product\(^8\)\(^-\)\(^9\). In spite of numerous observations, the oxidation of organic sulphur compounds by metal oxidants such as V(V) and Fe(III) has received little attention, perhaps because the one electron transfer nature of the V(V) or Fe(III) species present in solution is largely dependent on the environmental conditions. In this note, we present the results of kinetic studies of the title reaction and show that the one electron transfer oxidant has a pronounced effect on the mechanism of oxidation of (phenylthio)acetic acids.

**Experimental**

(Phenylthio)acetic acids were prepared by the method of Lee and Chan\(^4\). Ammonium metavanadate, potassium hexacyanoferrate(III) and all the other reagents used were of commercial AR grade. Reactions were carried out under pseudo-first order conditions by keeping an excess ($x \geq 15$ or greater) of [substrate] over [oxidant]. The reactions were followed by measuring the [oxidant] spectrophotometrically in JASCO-340 spectrophotometer. The pseudo-first order rate constant, $k_{obs}$, was determined from log[oxidant] versus time plot by the method of least squares. Duplicate runs showed that the rate constants were reproducible within $\pm 3\%$.

The stoichiometry of both the reactions were determined by allowing excess of oxidant to react with (phenylthio)acetic acid under reaction conditions. Estimation of unreacted [oxidant] spectrophotometrically after completion of the reaction revealed that the stoichiometry was 1:1 in the case of vanadium(V) and 1:2 in the case of iron(III). The major product, isolated after removing the solvent by distillation under reduced pressure, in the case of vanadium(V) oxidation, was identified as diphenyldisulphide by melting point and IR frequency. In the case of iron(III) oxidation, the product was the corresponding sulphone, which was confirmed by melting point and IR frequency.

**Results and discussion**

The first order dependence of the reaction on [oxidant] in both the cases is obvious from the linearity (correlation coefficient = 0.990) of the plot of log[oxidant] versus time. For example, if i) [substrate] $= 0.10 \text{ mol dm}^{-3}$, [vanadium(V)] $= 0.0030 \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.1 \text{ mol dm}^{-3}$, solvent $= 60:40 \text{ (v/v)}$ AcOH-$\text{H}_2\text{O}$ and temp. $= 40^\circ\text{C}$, the $k_{obs}$ value is $8.87 \times 10^{-4}\text{ S}^{-1}$ and correlation coefficient is 0.996 and ii) if [substrate] $= 0.050 \text{ mol dm}^{-3}$, 

\(^*\) Present address: Department of Chemistry, Adhiyamaan College of Engg., Hosur 635 109.
[iron(III)] = 0.0020 mol dm⁻³, [H⁺] = 0.66 mol dm⁻³, solvent = 50:50 (v/v) AcOH-H₂O and temp. = 35°C, the kobs value is 5.52 × 10⁻³ s⁻¹ and correlation coefficient is 0.994.

The proportional increase in the rate with the increase in [substrate] in both the cases is in conformity with the fact that the order in substrate is unity. It further gains evidence from the linearity of the plot of log kobs versus log [substrate] with a unit slope. The oxidation rate increases with increase in [acid] in both the cases. The order in [acid] is two and one in the case of vanadium(V) and iron(III) oxidations respectively.

In both the cases, addition of few drops of acrylonitrile under nitrogen atmosphere to the reaction mixture gives white polymeric product, indicating the participation of free radicals in these reactions.

The rate constants for the oxidation of few para-substituted (OCH₃, CH₃, F, CI, Br and I) (phenylthio)acetic acids correlate well with the Hammett’s substituent constants giving a ρ value of -3.64 and -1.22 at 35°C for vanadium(V) and iron(III) oxidation respectively. The negative ρ value indicates that the transition state is electron deficient as compared to the (phenylthio)acetic acid.

Studies of the effect of temperature on the rate constants for the unsubstituted (phenylthio)acetic acid gave the following activation parameters: For vanadium(V) oxidation ΔH² = 29 kJ mol⁻¹ and ΔS² = -142 JK⁻¹ mol⁻¹; and for iron(III) oxidation ΔH² = 73 kJ mol⁻¹ and ΔS² = -16 JK⁻¹ mol⁻¹.

Mechanism
For vanadium(V) oxidation - Initially prepared ammonium metavanadate in aqueous perchloric acid gives VO₂⁺ species as in Eq. (1)

\[
\text{NH₄VO₃} + 2H⁺ \rightarrow \text{NH₄}^+ + \text{VO₂}^+ + H₂O
\]  \hspace{1cm} (1)

On the basis of the forgoing kinetic picture, the following mechanism(Scheme 1) and rate law, Eq. (2), may be proposed

\[
\begin{align*}
K_1 & \quad \text{VO₂}^+ + 2H⁺ \rightarrow \text{VO₂}^+ + H₂O \\
C₆H₅S^+ + H₂O & \rightarrow \text{C₆H₅S}^+ \text{CH₂COOH} + \text{V(Ö)}^+
\end{align*}
\]

\[\text{H₂O} \quad \text{Complex} \rightarrow \text{C₆H₅S}^+ + \text{HOC}_2\text{COOH} + \text{V(Ö)}^+\]

Fast, \(k_1\)

Fast

Constant decomposition of the vanadium(V) species is confirmed by the formation of blue colouration.

Formation of a highly structured intermediate in the slow step is also in agreement with the high negative entropy of activation for this process. The intermediate would likely undergo solvolysis in a rapid reaction forming thiophenoxyl radical, glycollic acid and vanadium(IV). Formation of glycollic acid is confirmed by a spot test. Vanadium(IV) species is confirmed by the formation of blue colouration.

For iron(III) oxidation - Under the given acidic conditions, the reaction obeys the following simple mechanism (Scheme 2) involving the formation of a sulphur radical cation intermediate.

\[
\begin{align*}
K_1 & \quad \text{Fe(CN)}₆^{3-} + H⁺ \Leftrightarrow \text{H[Fe(CN)}₆^{3-}\]
C₆H₅S+CH₂COOH + H[Fe(CN)₆]³⁻ & \rightarrow \text{C₆H₅S}^+ \text{CH₂COOH} \\
\text{Slow} & \quad \text{Fast} \\
\text{C₆H₅S}^+ \text{CH₂COOH} + \text{H[Fe(CN)₆]}³⁻ & \rightarrow \text{C₆H₅S}^+ \text{CH₂COOH} + \text{H[Fe(CN)₆]}³⁻
\end{align*}
\]

Solvolysis

\[
\text{C₆H₅S}^+ \text{CH₂COOH} \rightarrow \text{C₆H₅SOCH₂COOH}
\]

Scheme 2
Rate law for the Scheme 2 is given by Eq. (3)

\[ k_{\text{obs}} = -\frac{d[\text{Fe(CN)}_6^{3-}]}{dt} = \frac{1}{[\text{Fe(CN)}_6^{3-}]} = K_1 k_2 [\text{Sulphide}][H^+] \] (3)

The alternate idea, the possibility of complex followed by solvolysis yielding sulphoxide as end product is ruled out because \( \text{Fe(CN)}_6^{3-} \) is substitution inert (low spin) and there is negligible loss of entropy. The formation of sulphur radical cation followed by sulphonium ion is already proposed in one of our earlier work involving organic sulphides and hexacyanoferrate(III). It is interesting to note that the products are different in these vanadium(V) and iron(III) oxidation of (phenylthio)acetic acid even though the reactions followed radical mechanism.

References