

## Studies on electron transfer reactions: Reduction of heteropoly 10-tungstodivanadophosphate by thioglycolic acid in aqueous medium

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**Abstract.** Rates of electron transfer reaction of thioglycolic acid with vanadium(V) substituted Keggin-type heteropolyanion,  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$ , in acetate–acetic acid buffers have been measured spectrophotometrically at 25°C. The order of the reaction with respect to substrate and oxidant is unity. The reaction shows simple second order kinetics at constant pH. The rate of the reaction increases with increase of pH of the medium. The mono-anion  $\text{HSCH}_2\text{COO}^-$  and di-anion  $^-\text{SCH}_2\text{COO}^-$  are found to be the reactive species. Rate constants for mono-anion and di-anion are evaluated from rate law derived from the mechanism. By applying Rehm–Weller relationship, self exchange rate constant for the  $^-\text{SCH}_2\text{COO}^-/\text{SCH}_2\text{COO}^-$  couple was evaluated as  $3.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25°C.

**Keywords.** Thioglycolic acid; heteropoly 10-tungstodivanadophosphate; outer sphere electron transfer reactions; Marcus theory; Rehm–Weller relationship.

### 1. Introduction

Oxidation of aliphatic thiols in aqueous medium is an important reaction in biochemistry. There are diverse mechanisms for thiol oxidation.<sup>1</sup> During the oxidation, the aliphatic thiol (RSH) may undergo oxidative dimerization to give the disulphide (RSSR) or may be oxidized to sulphinic acid ( $\text{RSO}_2\text{H}$ ) or sulphonic acid ( $\text{RSO}_3\text{H}$ ). A stronger oxidant oxidizes thiols to sulphonic acid whereas weaker oxidant oxidizes to disulphide. A number of factors such as self-exchange rates, pH, concentration ratio also play an important role in the oxidation of thiyl radical ( $\text{RS}\cdot$ ) generated in the initial step further to give sulphinic/sulphonic acids. Thioglycolic acid (TGA) is structurally simple. Oxidation of this substrate has been extensively studied to understand the mechanism of oxidation of biologically important thiols involved in physiological processes. With substitutionally labile oxidants, the oxidation of TGA proceeds through inner sphere mechanism in which a thermodynamically stable intermediate complex (MSR) is formed prior to the electron transfer. Inner sphere mechanisms<sup>2–9</sup> were reported for the oxidation of TGA by Mn(III), Ni(IV), Ni(III), V(V),

Ce(IV), Np(VI), Tc(VII), Mo(VI). With substitutionally inert oxidants such as  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ ,  $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$  and  $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$  outer sphere mechanism<sup>10–12</sup> is suggested for TGA oxidation.

Early transition metal oxygen clusters called heteropolyanions (HPA) are large and rapidly growing class of versatile and tunable oxidation catalysts. All the key molecular properties of these HPAs such as composition, size, shape, charge density, reduction potential can be systematically altered. HPAs can serve as tunable ligands for controlling the reactivity of transition metal ions. The metal vanadium exhibits several oxidation states, viz. +1, +2, +3, +4 and +5. Vanadium substituted HPAs are ideal candidates for the study of electron transfer reactions. In the present study, we report the kinetics of electron transfer reaction of TGA with heteropoly 10-tungstodivanadophosphate,  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$  in aqueous medium.

### 2. Experimental

The oxidant  $\text{K}_5[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$  was prepared by the method described by Domaille.<sup>13</sup> Thioglycolic acid is a commercial sample from Hi media and used as it is. All the reagents were prepared in

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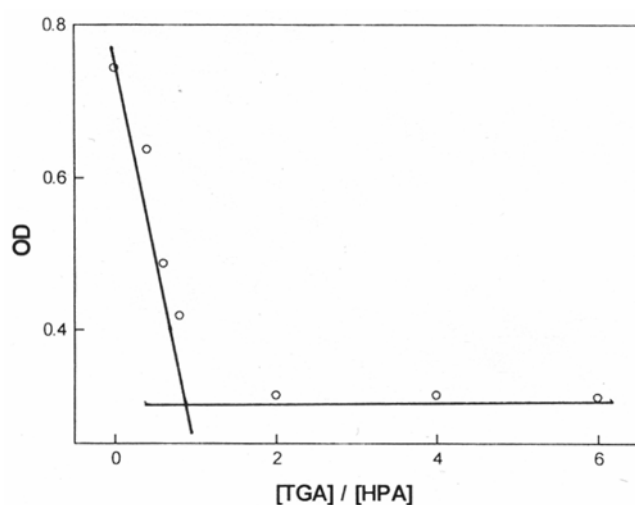
doubly distilled water. Carbonate free sodium hydroxide solutions were prepared and standardized by potassium hydrogen phthalate. Sodium acetate-acetic acid buffer were prepared by standard procedure and their pH was measured with Philips pH meter. Kinetic measurements were made using Schmadzu-1601 UV-Visible spectrophotometer fitted with thermostatic cell holder. The pseudo-first order rate constants were evaluated by the method of least squares from log optical density (OD) versus time plot.

### 3. Results and discussion

#### 3.1 Stoichiometry and products

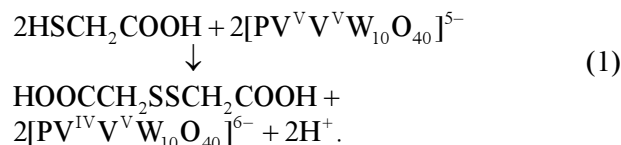
$[PV^V V^V W_{10} O_{40}]^{5-}$  was added to a solution containing TGA (0.02 M) in buffered medium of pH 4.8,  $5 \times 10^{-4}$  M of HPA, and kept for completion of the reaction and UV-visible spectrum was recorded. A new peak appears in the optical spectrum ( $\lambda_{max} = 660$  nm;  $\epsilon = 210 \text{ mol}^{-1} \text{ cm}^{-1}$ ). This spectrum matches with UV-visible spectrum of an electron reduced heteropoly blue (HPB)  $[PV^{IV} V^V W_{10} W_{40}]^{6-}$  reported in the literature.<sup>14</sup>

Solutions containing fixed amount of HPA ( $2.5 \times 10^{-4}$  M) and varying amount of TGA ( $1 \times 10^{-4}$  to  $15 \times 10^{-4}$  M) in sodium acetate-acetic acid buffer of pH 4.8 were prepared and OD was measured at 365 nm ( $\lambda_{max}$  of HPA) after completion of the reaction. Plot of OD versus the mole ratio  $[TGA]/[HPA]$ , (figure 1) shows that the stoichiometry of the



**Figure 1.** Spectrophotometric titration of TGA with  $[PV^V V^V W_{10} O_{40}]^{5-}$  ( $2.5 \times 10^{-4}$  M HPA in sodium acetate-acetic acid buffer of pH 4.8 at 25°C).

reaction is 1 : 1. The reaction of TGA with the HPA can be represented as

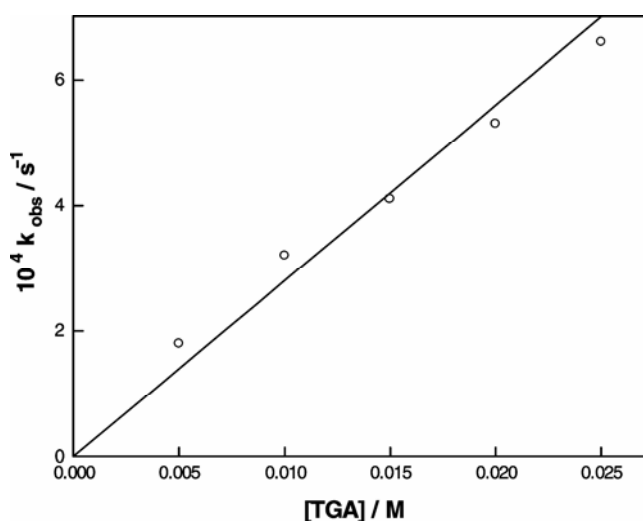


For the formation of sulphonic acid  $HOOCCH_2SO_3H$ , a mole of substrate will consume six moles of oxidant. The 1 : 1 stoichiometry rules out the oxidation of intermediate thiyl radical to sulphonic acid.

#### 3.2 Kinetics

The rates of electron transfer reaction between HPA and TGA were measured under pseudo-first order conditions ( $[TGA] > [HPA]$ ) in sodium acetate-acetic acid buffer of pH 4.58 at 25°C in an aqueous medium by measuring the decrease in OD of HPA at 365 nm. Plot of  $\log A_t$  versus time ( $A_t = OD$  at time  $t$ ) is linear. This shows that the order of the reaction with respect to  $[HPA]$  is one. The pseudo first order rate constant,  $k_{obs}$ , increases with an increase of  $[TGA]$ . Plot of  $k_{obs}$  versus  $[TGA]$  is linear (figure 2) and passes through origin. The order with respect to  $[TGA]$  is also one and the reaction shows simple second order kinetics with experimental rate law (2) at constant pH.

$$-d[HPA]/dt = k[HPA][TGA]. \quad (2)$$

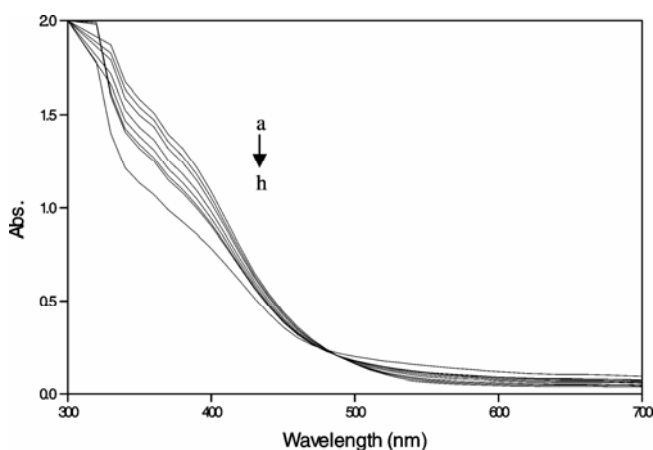


**Figure 2.** Plot of  $k_{obs}$  vs  $[TGA]$  for the reduction of  $[PV^V V^V W_{10} O_{40}]^{5-}$  by TGA at 25°C ( $[HPA] = 5 \times 10^{-4}$  M, pH = 4.58).

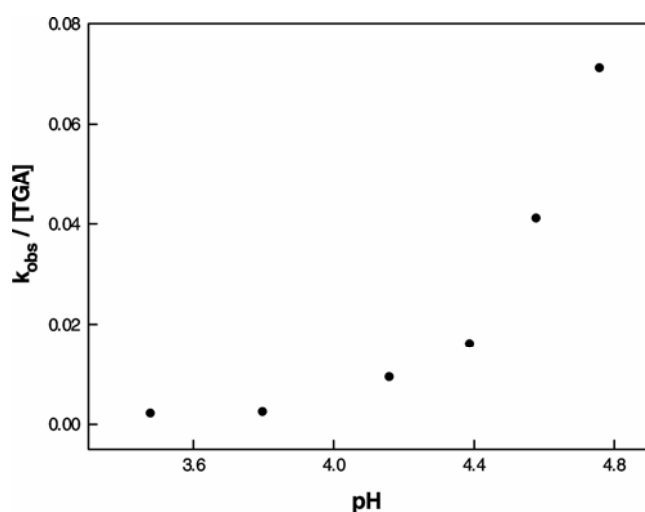
### 3.3 Mechanism

There is no detectable intermediate during the course of the reaction. Time dependent UV-visible spectra (figure 3) of the reaction mixture show a well-defined isobestic point at 492 nm. It is highly probable that the reaction may proceed through outer sphere mechanism.

The rates of the reaction were also measured in sodium acetate–acetic acid buffers of several pH values at 25°C. The pH-rate profile (figure 4) shows



**Figure 3.** Time dependent UV-visible spectra for the reduction of  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$  by TGA at 25°C ( $[\text{HPA}] = 5 \times 10^{-4}$  M,  $[\text{TGA}] = 0.02$  M,  $\text{pH} = 4.58$ ). Spectra recorded (a) 1 min, (b) 3 min, (c) 6 min, (d) 8 min, (e) 10 min, (f) 13 min, (g) 15 min and (h) 18 min after commencement of the reaction.



**Figure 4.** pH-rate profile for the reduction of  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$  by TGA at 25°C (pH maintained by sodium acetate–acetic acid buffer).

that as the pH of the medium increases,  $k_{\text{obs}}$ , also increases. This indicates that the deprotonated species which are more reactive than unprotonated species are involved in the reaction. TGA is a dibasic acid and the dissociation equilibrium has  $\text{pK}_a$  value of 3.53 and 10.10 for the carboxylic group and sulphydryl group respectively.<sup>15</sup>

The undissociated ( $\text{HSCH}_2\text{COOH}$ ) form of TGA is practically unreactive. For the mechanism shown in the scheme 1, the following rate law can be derived.

$$\frac{d[\text{HPA}]}{dt} = \frac{2\{k_a K_{a_1} [\text{H}^+ + k_b K_{a_1} K_{a_2}]\} [\text{TGA}]_t [\text{HPA}]}{[\text{H}^+]^2 + K_{a_1} [\text{H}^+] + K_{a_1} K_{a_2}} \quad (3)$$

The simplified rate law is

$$\frac{k_{\text{obs}}}{[\text{TGA}]_t} = 2k_a K_{a_1} / [\text{H}^+] + 2k_b K_{a_1} K_{a_2} / [\text{H}^+]^2 \quad (4)$$

By nonlinear least square fitting of rate data in several pH values, the rate constants  $k_a$  and  $k_b$  for the mono-anion and dianion of TGA were evaluated and presented in table 1 along with literature data for TGA oxidation by outer sphere oxidants  $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$  and  $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ . Examination of data in table 1 shows that the reactivity of the di-anion  $^-\text{SCH}_2\text{COO}^-$  is much more higher than that of mono-anion  $\text{HSCH}_2\text{COO}^-$ .

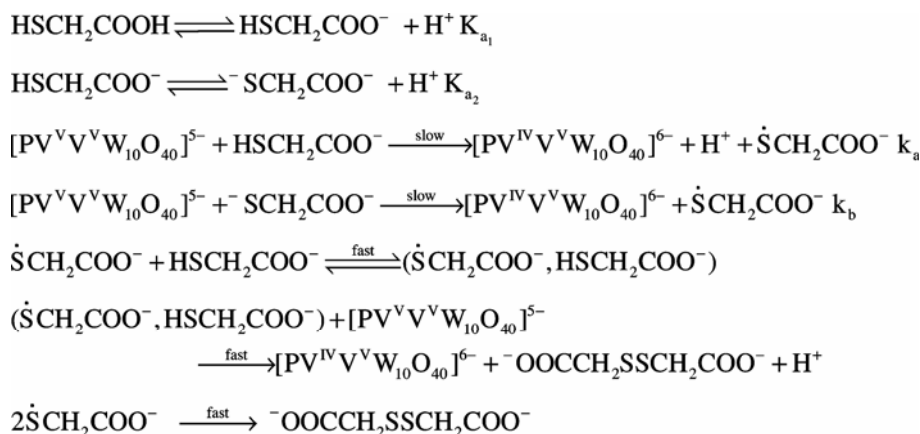
### 3.4 Marcus theory

The rate constant  $k_b$ , for TGA corresponds to a genuine outer sphere electron transfer process. Therefore, the application of cross relationship of Marcus theory may be made. The rate constant  $k_{12}$  for outer sphere electron transfer of cross reaction is related to the self-exchange rate constants  $k_{11}$ ,  $k_{22}$  of the reactants and to the equilibrium constant,  $K_{12}$ , of the reaction.

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{0.5} W_{12}, \quad (5)$$

where  $f_{12}$  is a term related to ionic strength of medium and  $W_{12}$  is the electrical work term.

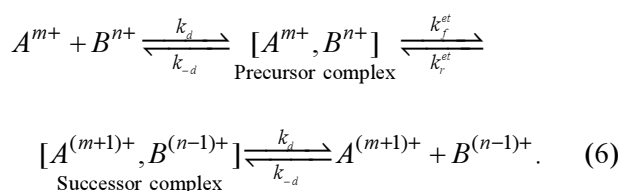
During outer sphere electron transfer reaction, the reactants collide to form precursor complex. Chemical activation followed by electron transfer leads to successor complex which separates into products by diffusion.



Scheme 1.

**Table 1.** Rate constants for the electron transfer reaction of mono and di-anion of TGA with outer sphere oxidants at 25°C.

Oxidant	$E^0$ (NHE)/V	$k_a/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_b/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Ref.
$[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$	0.89	53	$3.5 \times 10^6$	11
$[\text{Mo}(\text{CN})_8]^{3-}$	0.75	0.95	$1.85 \times 10^4$	12
$[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$	0.61	$0.69 \times 10^{-3}$	$2.74 \times 10^2$	This work



In principle, any one of the three processes will be the rate-limiting step.<sup>16</sup> Figure 5 is the theoretical plot of  $E^0$  versus  $\log k_{12}$  based on Marcus theory. There are two zones of diffusion control with slope  $0 \text{ V}^{-1}$  and  $16.6 \text{ V}^{-1}$  respectively with an intermediate zone of activation control with slope of  $8.3 \text{ V}^{-1}$ .

If the formation of precursor complex is slow, the rate of the reduction will be diffusion controlled and rate will be independent of  $E^0$  of oxidant (slope =  $0 \text{ V}^{-1}$ ). The diffusion controlled rate constant can be calculated by Debye equation

$$k_{\text{diff}} = \frac{8RT}{3\eta} \quad (7)$$

At 25°C,  $\eta = 0.01 \text{ P}$ , and  $k_{\text{diff}} = 6.6 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . The rate constants (table 1) are lower than this. Therefore, formation of precursor complex is not rate-limiting step. Either electron hop or diffusional separation into product will be the rate limiting step.

For  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}/[\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{6-}$  couple  $E^0$  value was reported as  $0.61 \text{ V}$  by Smith and Pope.<sup>17</sup> The plot of  $\log k_b$  vs  $E^0$  of oxidant is linear (figure 6) with slope of  $14.7 \text{ V}^{-1}$ , which is close to the theoretical slope  $16.6 \text{ V}^{-1}$ . This concludes that oxidation of TGA by these oxidants, diffusional separation of successor complex into product is the rate-limiting step with no tendency to observe rate-limiting electron hop. Perhaps with more powerful oxidants, 'activation domain' may become rate limiting.

The self exchange rate constants for outer sphere electron transfer reactions can be calculated by Rehm-Weller relationship.<sup>18,19</sup>

$$\Delta G_{12}^\ddagger = \frac{\Delta G^0}{2} + \left[ \left( \frac{\Delta G^0}{2} \right)^2 + \left( \frac{\Delta G_{11}^\ddagger + \Delta G_{22}^\ddagger}{2} \right)^2 \right]^{1/2} \quad (8)$$

Klinger and Kochi<sup>20</sup> have reported that this calculation gives more reliable results than Marcus equation.

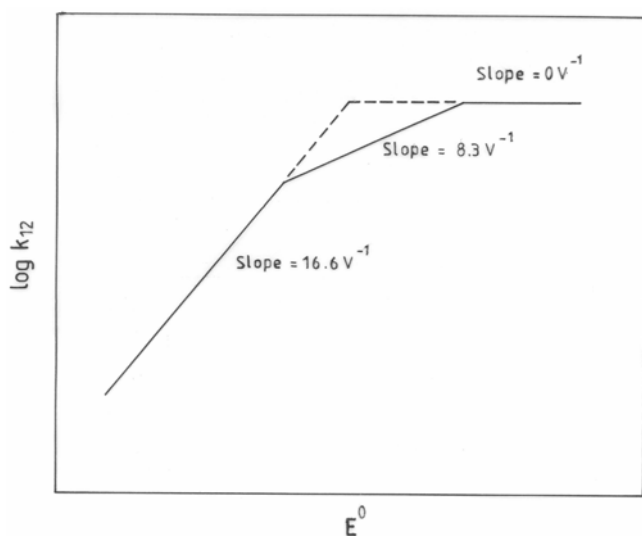
For evaluation of self-exchange rate constant for the couple  $^-\text{SCH}_2\text{COO}^-/\dot{\text{S}}\text{CH}_2\text{COO}^-$ , a knowledge of self exchange rate constant is needed for the couple  $[\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{6-}/[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$ . Sami and Raja-

sekaran<sup>21</sup> have reported  $k_{12} = 23 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for NADH oxidation by  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$ . Carlson *et al*<sup>22</sup> have reported self-exchange rate constant of NADH/NADH<sup>+</sup> couple as  $9 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  with  $E^0 = 0.93 \text{ V}$ . Employing this data and using  $E^0 = 0.61 \text{ V}$  for the oxidant, self exchange rate constant of  $[\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{6-}/[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$  was evaluated as  $k_{11} = 185 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Using this value, along with data in table 1, self exchange rate constant of  ${}^-\text{SCH}_2\text{COO}^-/\dot{\text{S}}\text{CH}_2\text{COO}^-$  can be evaluated. For this,  $E^0$  of  ${}^-\text{SCH}_2\text{COO}^-/\dot{\text{S}}\text{CH}_2\text{COO}^-$  is needed. For the couple<sup>23</sup> (mono-anion)  $\text{HSCH}_2\text{COO}^-/$

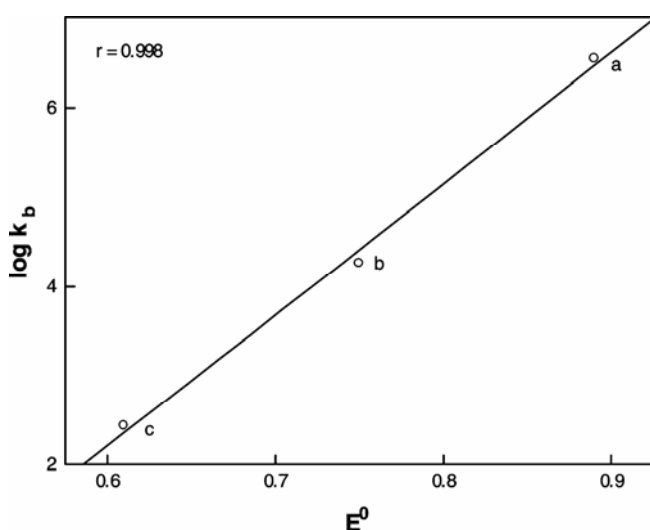
$\dot{\text{S}}\text{CH}_2\text{COO}^-$ ,  $E^{0'}$  value is 1.34 V. For the couple (di-anion)  ${}^-\text{SCH}_2\text{COO}^-/\dot{\text{S}}\text{CH}_2\text{COO}^-$ ,  $E^0$  value calculated from (9) is 0.735 V.

$$E^0 = E^{0'} + 0.059 \log K_{a_2} \quad (9)$$

( $K_{a_2}$  is the dissociation constant of thiol group of TGA). The self exchange rate constant for the couple  ${}^-\text{SCH}_2\text{COO}^-/\dot{\text{S}}\text{CH}_2\text{COO}^-$  was evaluated using Rehm–Weller relationship and found to be  $3.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25°C. For the oxidation of TGA by  $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ , using self exchange rate constant<sup>24</sup> of oxidant a value of  $3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , along with data in table 1, Rehm–Weller relationship gives self-exchange rate constant for  ${}^-\text{SCH}_2\text{COO}^-/\dot{\text{S}}\text{CH}_2\text{COO}^-$  couple as  $6.1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The value evaluated by us agrees with literature data.<sup>12</sup>



**Figure 5.** Theoretical plot of  $\log k_{12}$  vs  $E^0$  based on Marcus theory.



**Figure 6.** Plot of  $\log k_b$  vs  $E^0$  of oxidants for the oxidation of TGA. ( $a = [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ ;  $b = [\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ ;  $c = [\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$ ).

#### 4. Conclusion

TGA undergoes facile one electron transfer reaction with vanadium(V) substituted Keggin-type heteropolyanion  $[\text{PV}^{\text{V}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{5-}$  in aqueous acid medium at ambient temperature. Oxidation of TGA follows simple second order kinetics. In the pH range employed, the active species of TGA are  $\text{HSCH}_2\text{COO}^-$  and  ${}^-\text{SCH}_2\text{COO}^-$ . The one electron transfer proceeds through outer sphere mechanism in which the diffusional separation of product is the rate limiting step. We hope that the results of the present work may facilitate the application of Marcus theory to the oxidation of TGA by outer sphere oxidants in future.

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