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Kinetics and Mechanistic Studies of Oxidation of Thioglycolic Acid by Manganese(III)

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Kinetic and mechanistic studies of oxidation of thioglycolic acid by manganic pyrophosphate is extensively studied at various temperatures to evaluate the thermodynamic parameters and stability constant of the intermediary complex. Second order rate constants obtained in these investigations are utilised to correlate the effects of [Thioglycolic acid], [manganese(III)], dissociated [H^+], total [SO_4^{2-}], total [$P_2O_7^{4-}$] and added [manganese(II)]. The mechanism of the reaction involved the formation of a transitory intermediate 1 : 1 cyclic complex and the disproportionation of the complex through a S—H bond cleavage is the rate determining step. The sulphur containing ion-free radicals dimerise to yield disulphide as the end-oxidation product which is a general observation in the oxidation of α-mercapto carboxylic acids by transition metal ions. Various thermodynamic factors such as $\Delta E^{\#}$, $-\Delta H^{\#}$, $\Delta F^{\#}$, $\Delta S^{\#}$ and frequency factor (A) are calculated

INTRODUCTION

Much of the current interest in electron transfer reactions between metal ions and organic compounds containing sulphydryl and polarisable hydroxyl groups is due to the expectation that these may serve as model systems for studying the biochemical redox reactions since many active sites of redox enzymes are thought to involve both, a sulphur atom and a metal ion.

Earlier studies[1, 2] have involved ceric ion oxidation of α-hydroxy acids. The formation of a complex between organic substrates and the oxidant has been postulated with its subsequent decomposition to yield an organic free radical and reduced metal ion. The extension of these investigations to the α-mercapto carboxylic acids where the intermediary complex involve metal ion-sulphur co-ordination, was studied in detail in 1968 by Hill and McAuley[3]. No such kinetic investigations were previously undertaken possibly owing to the need to use fast reaction techniques to follow these oxidation reaction rates. In these investigations Hills McAuley[3] have observed that the oxidation producing radical intermediates are well known in sulphur systems. The greater stability of these sulphur-containing radicals was also demonstrated by the fact that in most cases these α-mercapto acids yield disulphide as final product.

A survey of literature shows that none has attempted the oxidation of mercapto carboxylic acids with manganese(III). In order to establish probable pathways of oxidation with manganese(III) as an oxidant a detailed kinetic study is undertaken.

EXPERIMENTAL

The materials employed were of the highest purity available. A solution of manganese(III) pyrophosphate was prepared by the method of Gmelin[4] and was standardised against iron(II) using diphenylamine sulphonate as an internal indicator and also to a potentiometric end-point. The solutions of thioglycolic acid (TGA) were standardised adopting the procedures described in the literature[5–7].

STOICHIOMETRY

Under the experimental conditions of kinetic runs *viz.* $[H^+] = 1.0$ N, $[SO_4^{2-}] = 0.5$ M and $d[P_2O_7^{4-}] = 2.0 \times 10^{-2}$ M, it was observed that one mole of thioglycolic acid consumes six equivalents of manganese(III) for its complete oxidation to give sulpho-acetic acid as the end-product. The formation of this end-product *i.e.*, sulpho-acetic acid was also confirmed by a spot test[8]. The stoichiometry may be written as

$$HS\cdot CH_2COOH + 6Mn(III) + 3H_2O \rightarrow HO_3SCH_2COOH + 6H^+ + 6Mn(II)$$

However when [Mn(III)] used is not in excess but almost equivalent to the required stoichiometric concentration, disulphide *i.e.*, dithioglycolic acid was found to be the end-product, which was also isolated and identified[3].

RESULTS AND DISCUSSION

The reaction follows simple second order kinetics under the conditions $[Mn](III) \simeq [TGA]$. A plot of $1/(a-x)$ vs. time (t) is linear indicating that the total order is two. At different [Mn(III)] and [TGA], the plot of $\frac{2.303}{(a-b)} \log \frac{(a-x)}{(b-x)}$ vs. time (t) is also linear indicating first order dependence each in [Mn(III)] and [TGA]. This is further confirmed by applying Dhar's equation[9].

The rate increases with increase in [TGA] under the conditions: $[Mn(III)] = 2.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0$ mol dm^{-3} at 35° ± 0.05°C. The plot of reciprocal of rate constant against the reciprocal of the initial [TGA] is linear. From the intercept and slope of this linear plot, the stability constant (K_f) of 1:1 Mn(III)-TGA complex has been evaluated under the experimental conditions stated above and found to be $K_f = 39.16$ dm^3 mole^{-1}.

The rate of oxidation decreases by two and a half times for a two-fold increase of [Mn(III)], i.e., 2.52 dm^3 mole^{-1} min^{-1} at 3.0×10^{-2} mol dm^{-3} [Mn(III)]. However with the increase of [Mn(III)] the initial rate proportionately increases. This type of acceleration effect in the initial rate may be due to the availability of kinetically reactive manganese(III) species, *viz.* $Mn_4(P_2O_7)_3$ in the reaction mixture. It may be concluded that the reactive oxidant species forms a transient 1:1 cyclic complex with TGA.

The rate of oxidation increases with increase in $[H^+]$. It is evident from Fig. 1A that with the increase of $[H^+]$, in the range of 0.75 N to 1.50 N, the rate constant proportionately increases; however, with further increase of $[H^+]$ beyond 1.50 N the rate is not affected and remains constant. This type of acceleration effect may be explained considering the protonation of the displaced pyrophosphate ($HP_2O_7^{3-}$). The hydrogen ion contributed from added sulphuric acid protonates the displaced pyrophosphate $HP_2O_7^{3-}$ ligand from manganic pyrophosphate,

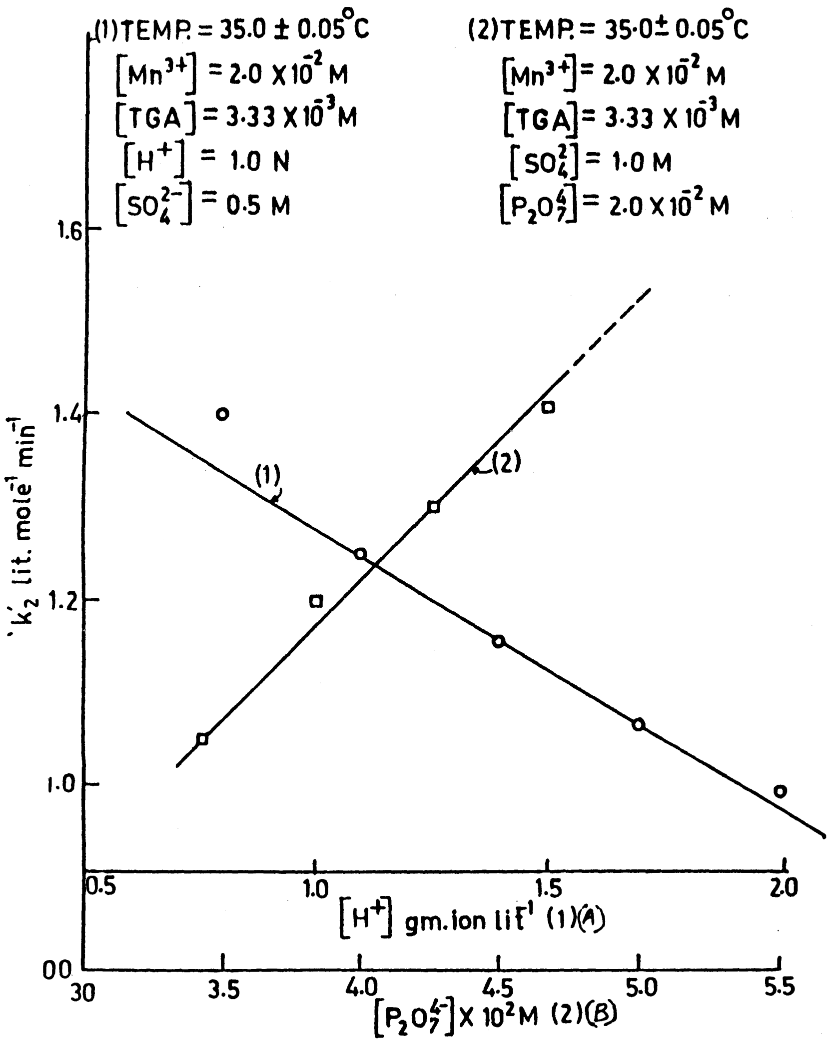


Fig. 1 Thioglycolic acid–Mn^{3+} reaction: Effect of variation of dissociated $[H^+]$ and $[P_2O_7^{4-}]$ on second order rate constant ['k_2']

thereby facilitating the formation of more and more 1:1 transient complex. However, a retardation effect with increase in [$P_2O_7^{4-}$] is noticed (Fig. 1B). This may be due to the total [$P_2O_7^{4-}$] present in the reaction mixture, which inhibits the formation of intermediary cyclic complex.

The rate of oxidation increases with increase in total [SO_4^{2-}] (Fig. 2A). This may be attributed to the displacement of co-ordinated pyrophosphate ligand

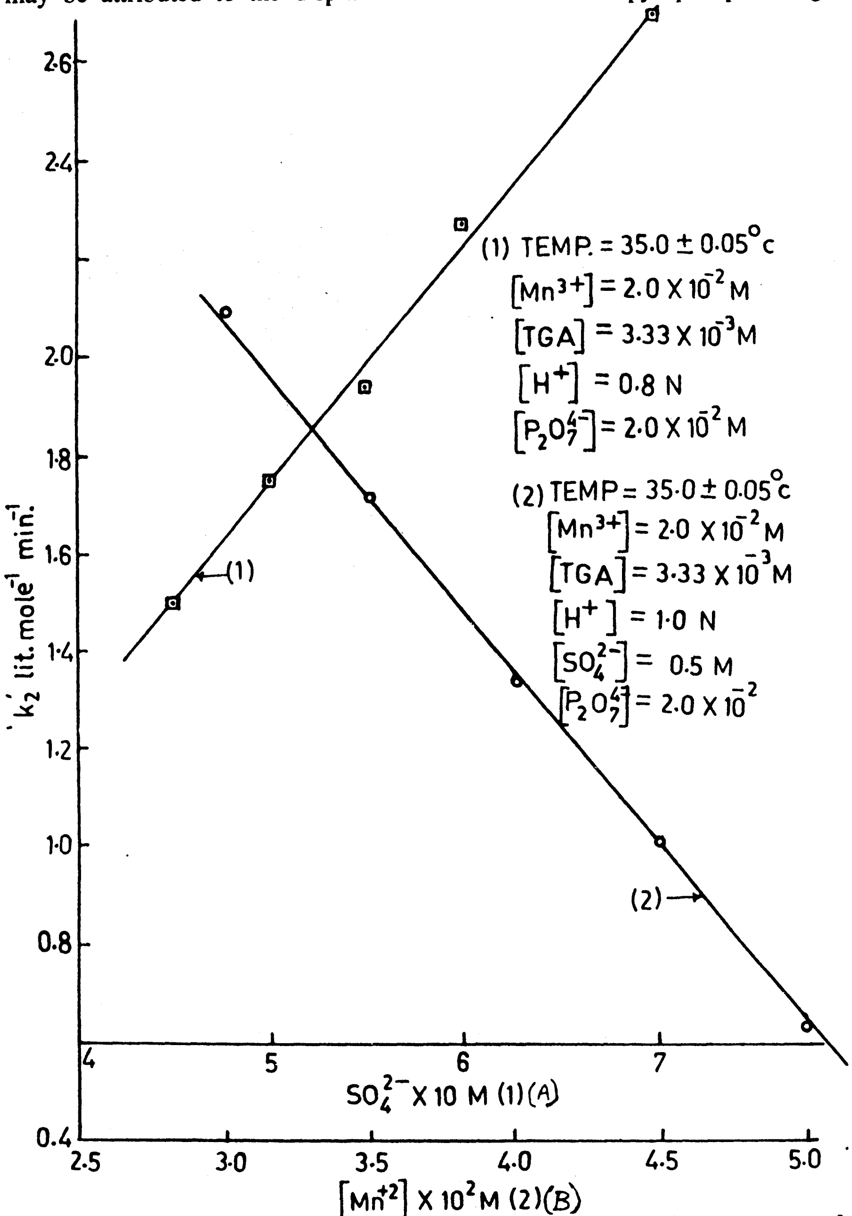
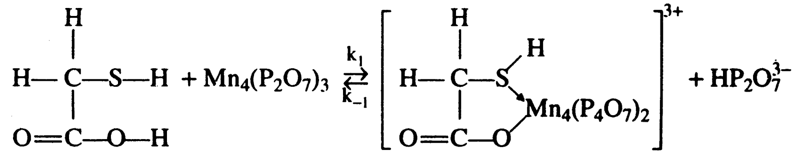


Fig. 2 Thioglycolic acid–Mn^{3+} reaction: Effect of variation of total [SO_4^{2-}] and added [Mn^{2+}] on second order rate constant ['k_2']

leading to the establishment of new Mn(III)-Mn(II) couple with $[SO_4^{2-}]$ as a ligand. It is well known that such a redox couple has a higher redox potential and more oxidation power than the pyrophosphate as a ligand. Added Mn(II) decreases the rate of oxidation (Fig. 2B). This may probably be due to the fact that Mn(II) competes with Mn(III) to form a more stable complex with TGA. Such instances are indeed encountered in the literature[10].

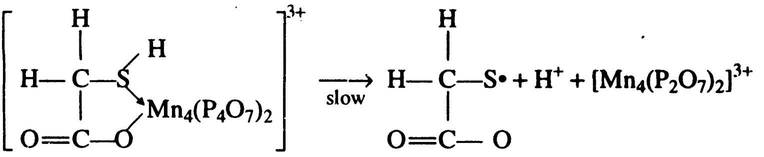
A series of kinetic runs were carried out at five different temperatures. The energy of activation ($\Delta E^{\#}$), enthalpy of activation ($-\Delta H^{\#}$), free energy of activation ($\Delta F^{\#}$), entropy of activation ($\Delta S^{\#}$) and frequency factor (A) are also calculated and found to be 9.594, 9.524, -2.175 Kcal mole^{-1}, 27.69 e.u. and 8.0×10^{11} sec^{-1} respectively.

Based on the above experimental observations and thermodynamic parameters, the following mechanism is proposed. The first and second dissociation constants reported[11] for thioglycolic acid are 2.00×10^{-4} and 2.10×10^{-11} at 25°C. The magnitude particularly that of second one is negligibly small. In acid medium, therefore, one would normally expect thioglycolic acid to remain practically in an undissociated form. Since the end-product of oxidation of thioglycolic acid in kinetic runs is dithioglycolic acid it is obvious that —SH group may provide a reaction site. Further if the sulphur atom of the α-mercaptocarboxylic acids is involved in the formation of a co-ordinate bond with manganese(III) ion, it can be visualised that the real S—H bond-energy in the intermediary complex may be a little lower than its theoretical bond-energy value and also lower than that of a C—C bond-energy. The following mechanism may be in agreement with the experimental observations.

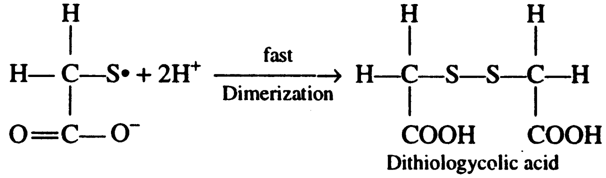


(1)

The coordinated intermediary complex may disproportionate to give ion-free radical as shown in Eq. (1).

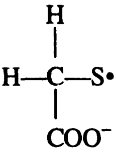


(2)



$$\mathrm{HOOC{-}CH_2{-}S^{\bullet}} + 2H^+ \xrightarrow[\text{Dimerization}]{\text{fast}} \mathrm{H_2C(COOH){-}S{-}S{-}CH_2(COOH)} \quad (3)$$

This mechanism is based on the initial reversible electron transfer process, similar to the one proposed by Harynes, Turner and Waters[12] and also Fieser[13]

The possiblity of the formation of ion-free radical  $H{-}\overset{\displaystyle H}{\underset{\displaystyle COO^-}{C}}{-}S\bullet$ is evidenced by the ability of polymerisation of acrylonitrile or reduction of mercuric chloride. This was also supported by the observation of Kolthoff and Meehan[14].

The corresponding rate law in consonance with the above observations may be written as

$$\frac{-d[Mn^{3+}]}{dt} = \frac{k_2K_f[Mn^{3+}]\,[\text{thiologycolic acid}]}{1 + K_f\,[\text{thioglycolic acid}]}$$

where 'k_2' is the observed second order rate constant for the overall reaction while 'k_f' is the formation constant of the 1 : 1 intermediary cyclic complex.

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