Studies on the Oxygen Atom Transfer Reactions of Peroxomonosulfate: Oxidation of Lactic Acid

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ABSTRACT: Kinetics of oxidation of lactic acid by peroxomonosulfate (PMS) catalyzed by Ni(II) ions has been studied in aqueous buffered (sodium acetate-acetic acid) medium. The reaction follows first order in [PMS] and [Ni(II)] and inverse first order in [H^+]. The effect of pH on the rate suggests that both HSO_5^- and SO_5^{2-} are the active forms of the oxidant. The intermolecular reaction between HSO_5^- and nickel lactate results in hydroperoxide intermediate in the rate-limiting step. The deprotonated form of PMS, SO_5^{2-}, gives a lactate-nickel-peroxomonosulfate intermediate, which then undergoes intramolecular oxidation–reduction reaction. The thermodynamic parameters also support the kinetic scheme. Comparison with (nickel) glycolate shows that the electron-donating methyl group in lactic acid enhances the nucleophilic interaction of the α-hydroxyl group. A suitable mechanistic scheme is also proposed. © 2009 Wiley Periodicals, Inc. Int J Chem Kinet 41: 449–454, 2009

INTRODUCTION

Aliphatic alpha hydroxy acids are compounds of interest due to their occurrence and functions in human physiology. Lactic acid, 2-hydroxy propionic acid, in its crude form (sour milk) has been used since ancient days as a skin rejuvenating agent. Lactic acid is produced in the human body by anaerobic metabolism of glucose and plays a critical role in generating energy through the process known as the Cori cycle or lactic acid cycle [1]. Lactate is the preferred fuel source in highly oxidative tissues such as heart muscle and slow-twitch skeletal muscle fibers [2]. Lactic acid (LA) is a valuable component in athletic fluid replacement beverages. Thus the importance has led to the extensive investigations on the kinetics and mechanism of oxidation of lactic acid. The oxidation of glycolic acid, another alpha hydroxy acid, by peroxomonosulfate (PMS) in the presence of metal ions such as Ni(II) and Cu(II) ions at pH 4.05–5.89 has been reported from this laboratory [3]. The deprotonated form of PMS (SO_5^{2-}) reacts with nickel glycolate to give nickel glycolate peroxomonosulfate intermediate, which rearranges to a hydroperoxide by the oxygen atom transfer to the hydroxyl group of the chelated glycolic acid. At the experimental conditions, a major fraction (>99.99%) of peroxomonosulfate exists as HSO_5^- and we could not observe the reaction between the protonated form of the peroxide with the metal glycolate. This is probably because the nucleophilic interaction of the hydroxyl

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group (the reaction center of the metal glycolate) with the peroxide oxygen is made less favorable by the –I inductive effect of the hydrogen atoms at the alpha carbon. If it is so, one can expect that the substitution of the hydrogen atom by an electron-donating group may increase the probability of the reaction between nickel-α-hydroxy carboxylate and HSO_5^-. Thus the oxidation of lactic acid by PMS was carried out with an objective outlined previously, and the results are discussed in this report.

EXPERIMENTAL

Potassium salt of peroxomonosulfate, under the trade name Oxone® (Fluka Chemie, Buchs, Switzerland), was used as such, and no attempt was made to purify it further because all the previous attempts have been reported unsuccessful [4]. The purity of the sample was checked by cerimetry using ferroin indicator, and the absence of free hydrogen peroxide was ensured by a test with permanganate. Fresh solution of PMS was prepared daily and estimated by iodometry. DL-Lactic acid (85% aqueous solution) was from Alfa Aesar (Heysham, Lancashire, UK). The stock solution of lactic acid was prepared daily before starting the experiments and was standardized by alkalimetric titrations. Nickel(II) nitrate hexahydrate (S.D. Fine-Chem, Mumbai, India) is the source of Ni(II) ions. All other chemicals used were of the highest purity available.

The pH of the reaction mixture was maintained with a high concentration of buffer, usually with 0.32 M of OAc^-. The kinetics was carried out in buffered medium with a large excess of lactic acid over PMS in the temperature range 298–311 K. The reaction was followed by estimating the unreacted PMS as a function of time by the iodometric method. The liberated iodine was titrated against a standard sodium thiosulfate solution using starch as an indicator. The stoichiometry was determined at pH 4.05 by taking a large excess of [PMS] (0.04 M) over [LA] (0.005 M) and [Ni(II)] (4.0×10^{-4} M). The unreacted [PMS] was estimated after 24 h. A correction for the decomposition of PMS under identical conditions was applied. The product analysis was also carried out with a slight excess of stoichiometric [PMS], and the pH was adjusted to ~4.0 with lactate/lactic acid itself (instead of acetate/acetic acid).

The stoichiometry of the reaction can be represented as in Eq. (1).

$$\text{Lactic acid} + 2\,\text{PMS} \xrightarrow{\text{Ni(II)}} \text{Acetic acid} + CO_2 \uparrow \quad (1)$$

The formation of acetic acid was confirmed by the color test with lanthanum nitrate and iodine [5]. The evolution of carbon dioxide was confirmed with freshly prepared limewater. No gas evolution was observed when gaseous products were passed through sodium hydroxide solution, and this clearly showed that the gaseous product is only carbon dioxide. The formation of oxygen was also excluded by the color test with alkaline sodium dithionite activated with indigo carmine [6].

RESULTS AND DISCUSSION

The oxidation of lactic acid by PMS occurs only in the presence of Ni(II) ions. The concentrations of Ni(II) ions used in this study are in the range from $\sim 5.0 \times 10^{-4}$ to $\sim 10.0 \times 10^{-4}$ M. The kinetics was always carried out under the conditions [LA] $\gg$ [PMS] and [LA] $\gg$ [Ni(II)]. The rates of the reactions were measured by monitoring the concentrations of PMS as explained in the Experimental section. The rate is first order with respect to [PMS] as shown by the linear plots of $\log[\text{PMS}]_t$ vs. time. The plots are linear with high correlation coefficient ($r^2 > 0.98$) even at 80% conversion of [PMS]. The first-order rate constant values (k_{obs}) were calculated by the linear regression of time vs. log[PMS]. The effect of sulfate ion, the reduction product of PMS, on the rate is studied by calculating the k_{obs} values at different sulfate ion concentrations ranging from 0.025 M to 0.10 M. The results show that the added sulfate ion has no effect on the rate. However, all the kinetics was carried out only in the presence of the 0.05 M sulfate ion.

The effect of the metal ion concentration [Ni(II)] on the rate is studied at different pH and temperatures. An increase in [Ni(II)] causes a proportional increase in k_{obs}. The plots k_{obs} vs. [Ni(II)] (Fig. 1) are straight lines passing through origin or with a small negative intercept, which can be approximated (statistically) as through origin. The effect of the lactic acid concentrations on k_{obs} is studied by calculating k_{obs} values at different [LA], keeping [Ni(II)] and pH at constant values. Perusal of the results shows that the rate constant k_{obs} is independent of [LA] over the concentration range from 0.023 to 0.14 M. Similar result is observed at all pH values and temperatures. Thus k_{obs} obeys Eq. (2).

$$k_{\text{obs}} = k^1 \times [\text{Ni(II)}] \qquad (2)$$

The k^1 values are calculated at different pH values (4.05–5.89) and temperatures from k_{obs} vs. [Ni(II)] plots. Perusal of the k^1 values show that they increased with pH, and the plots $\log(k^1)$ vs. pH are almost straight lines with a positive slope in the range of 0.7–0.8. But

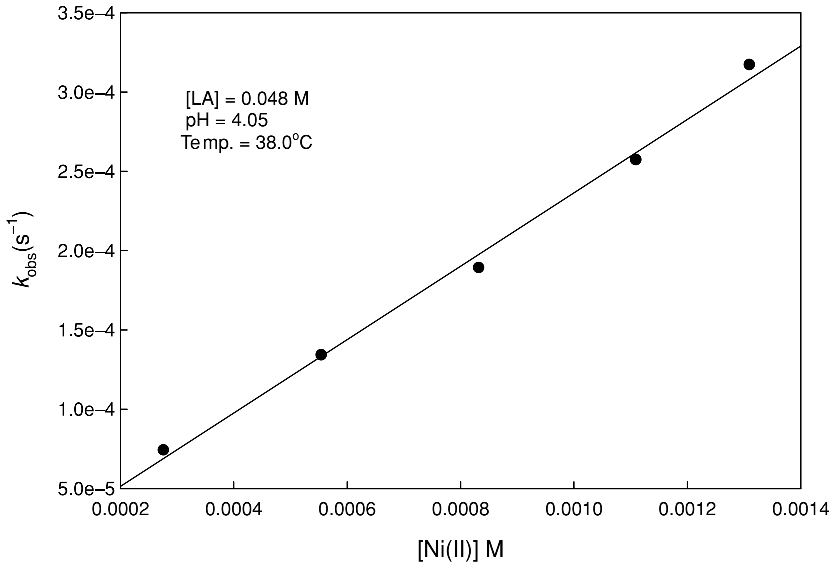

Figure 1 Plot of k_{obs} vs. [Ni(II)].

the plots k^1 vs. $[H^+]^{-1}$ are straight lines with a positive intercept (Fig. 2).

The effect of the acetate ion concentration on the rate is also studied at pH 4.05 and 4.75. At constant pH, the rate is not at all affected by the $[OAc^-]$ (0.08–0.32 M) and hence the reaction is not a base-catalyzed one. The added radical quenchers such as ethanol or tert-butanol (0.025–0.05 M) have no effect on the k_{obs} values. The ionic strength in the range from 0.15 to 0.30 M, adjusted with sodium nitrate, also has a negligible effect on the rate.

Based on the experimental results, we can propose the following kinetic scheme for the oxidation of lactic acid by PMS in the presence of Ni(II) ions:

$$CH_3CH(OH)COO^- + Ni(II) \overset{K_1}{\rightleftharpoons} \underset{(ML^+)}{CH_3CH(OH)COONi^+} \quad (3)$$

$$CH_3CH(OH)COONi^+ + HSO_5^- \overset{K_2}{\rightleftharpoons} CH_3CH(OH)COONiSO_5^- + H^+ \quad (4)$$

$$CH_3CH(OH)COONi^+ + HSO_5^- \xrightarrow{k_1} \text{Products} \quad (5)$$

$$CH_3CH(OH)COONiSO_5^- \xrightarrow{k_2} \text{Products} \quad (6)$$

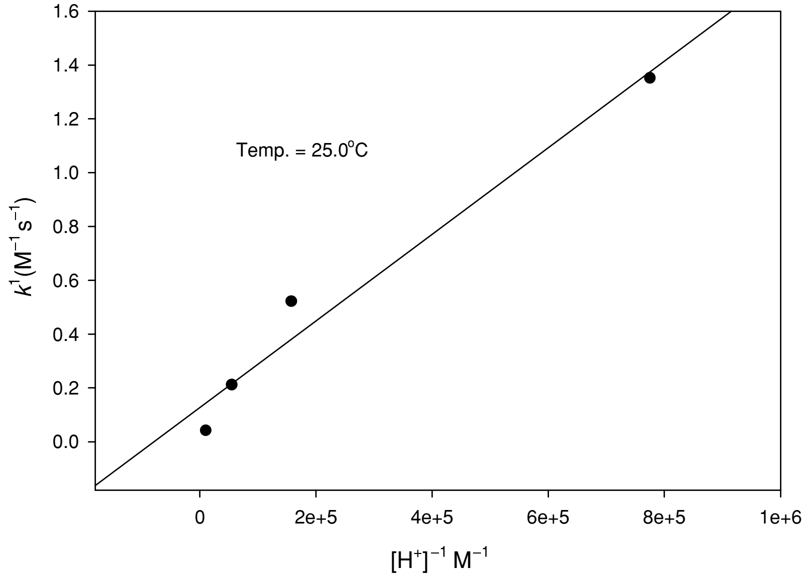

Figure 2 Plot of k^1 vs. $[H^+]^{-1}$.

The rate equation for the kinetic scheme in reactions (3)–(6) can be expressed as in Eq. (7).

$$\frac{-\mathrm{d}[\mathrm{PMS}]}{\mathrm{d}t} = (k_1 + k_2K_2/[\mathrm{H}^+])[\mathrm{ML}^+][\mathrm{PMS}] \qquad (7)$$

$$\therefore k_{\mathrm{obs}} = (k_1 + k_2K_2/[\mathrm{H}^+])[\mathrm{ML}^+] \qquad (8)$$

Lactic acid is a weak acid with pKa value of 3.45 (25°C) [7]. Alpha hydroxy acids react with Ni(II)ions to give 1:1 complex ML^+ in which the metal ion is bonded to the carboxylate oxygen [8–11]. Equation (3) represents the formation of the 1:1 complex in lactic acid–nickel system and the reported value for K_1 is 164.4 M^{-1} (25°C) [8]. This value is used in our calculations. Simple calculation shows that ∼90% of Ni(II) ion will be in the form of ML^+ at our experimental conditions. Because the concentrations of Ni(II) ions used in this study are very small compared to [LA], we can approximate $[\mathrm{ML}^+] \approx [\mathrm{Ni(II)}]_T$. Therefore, Eq. (8) can be modified as in Eq. (9).

$$k_{\mathrm{obs}} = (k_1 + k_2K_2/[\mathrm{H}^+])[\mathrm{Ni(II)}]_{\mathrm{T}} \qquad (9)$$

Comparison of Eq. (9) with Eq. (2) shows that k^1 can be expressed as in Eq. (10).

$$k^1 = k_1 + k_2K_2/[\mathrm{H}^+] \qquad (10)$$

Equation (10) explains all the experimental observations. The k_1 and k_2K_2 values and the corresponding thermodynamic parameters are listed in Table I. The radical quenchers ethanol and tert-butanol have no effect on the rate, and therefore the alcohol quenchable radical intermediates such as $\mathrm{OH}^\bullet$ and $\mathrm{SO}_4^{-\bullet}$ [12] are not produced in the reaction. This clearly shows the absence of a higher oxidation state of Ni(II) in the mechanism.

The equilibrium (4) can be expressed as the sum of the two equilibria (11) and (12). The literature value of K_{d} is 4.0×10^{-10} M at 25°C [13].

$$\mathrm{HSO}_5^- \overset{K_{\mathrm{d}}}{\rightleftharpoons} \mathrm{SO}_5^{2-} + \mathrm{H}^+ \qquad (11)$$

Table I The Kinetic and Thermodynamic Parameters

Temperature (°C)	k_1 ($\mathrm{M}^{-1}\mathrm{s}^{-1}$)	$10^6 \times k_2K_2$ (s^{-1})
25.0	0.13	1.61 (1.01)
31.0	0.22	2.27 (1.79)
38.0	0.64	4.42 (3.47)
$\Delta H^{\neq}$(kJ mol^{-1})	93.9	54.8 (69.5)
$\Delta S^{\neq}$(J K^{-1} mol^{-1})	52.5	−172.1 (−126.4)

Values in parentheses correspond to the nickel glycolate.

$$\mathrm{CH_3CH(OH)COONi}^+ + \mathrm{SO}_5^{2-} \overset{K_3}{\rightleftharpoons} \mathrm{CH_3CH(OH)COONiSO}_5^- \qquad (12)$$

Therefore, reactions (4) and (6) represent the oxidation of nickel lactate by SO_5^{2-}, whereas reaction (5) is by HSO_5^-. Results on the influence of alkali metal ion (M^+) in the oxidation reactions with PMS [14,15] have shown that SO_5^{2-}forms an ion pair with a metal ion M^+, whereas such a reaction with HSO_5^- is not observed. Therefore, it is reasonable to assume that SO_5^{2-} readily forms an ion pair with nickel lactate, which may be converted into reactive peroxide intermediate. The intramolecular electrophilic attack of the peroxide oxygen at the hydroxyl group may result in a hydroperoxide, and this reaction is represented in Eqs. (4) and (6). Therefore, reaction (6) is the intramolecular pathway for the oxidation and Eq. (5) is the intermolecular mechanism.

If we substitute reaction (4) with Eqs. (11) and (12), then the kinetic constant k_2K_2 becomes $k_2K_{\mathrm{d}}K_3$, where K_{d} is the dissociation constant of HSO_5^-. Therefore, $\Delta H^{\neq}$ corresponding to the kinetic constant k_2K_2 given in Table I can be expressed as $\Delta H^{\neq} = \Delta H^0_{K_{\mathrm{d}}} + \Delta H^{\neq}_{k_2K_3}$, where $\Delta H^0_{K_{\mathrm{d}}}$ is the enthalpy of dissociation for the equilibrium (11). Similarly, the $\Delta S^{\neq}$ can be written as the sum of $\Delta S^0_{K_{\mathrm{d}}}$and $\Delta S^{\neq}_{k_2K_3}$. Using the literature [13] values of $\Delta H^0_{K_{\mathrm{d}}}$ (20.93 kJ mol^{-1}) and $\Delta S^0_{K_{\mathrm{d}}}$ (−108 J $\mathrm{K}^{-1}\mathrm{mol}^{-1}$), $\Delta H^{\neq}_{k_2K_3}$and $\Delta S^{\neq}_{k_2K_3}$ values are calculated as 33.9 kJ mol^{-1} and −64.1 J K^{-1} mol^{-1}, respectively. Comparison of these values with those of nickel glycolate (48.6 kJ mol^{-1} and −18.4 J K^{-1} mol^{-1}) shows that that enthalpy of activation is lowered by ∼15 kJ mol^{-1} and the entropy of activation becomes more negative by ∼35 J K^{-1} mol^{-1}. This means that the formation of activated state is more favorable in nickel lactate than nickel glycolate. Lactic acid differs from glycolic acid only by the α-methyl group. That is, the substitution of a hydrogen atom at the alpha carbon by an electron-donating (+I) methyl group favors the nucleophilic interaction of the hydroxyl group with the peroxide oxygen.

The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for the reaction between nickel lactate and HSO_5^- are also shown in Table I. Perusal of the values shows that the enthalpy of activation is almost three times higher than that of the reaction with SO_5^{2-}. One interesting observation is that $\Delta S^{\neq}$ is positive and is very close to $-41 \cdot Z_A \cdot Z_B$ J K^{-1} mol^{-1} [16], the entropy of activation due to electrostatic effects for a reaction involving two ions of charges Z_A (+1) and Z_B(−1). This is in accordance with our kinetic scheme in which the activated state is mainly due to the (electrostatic) interaction between

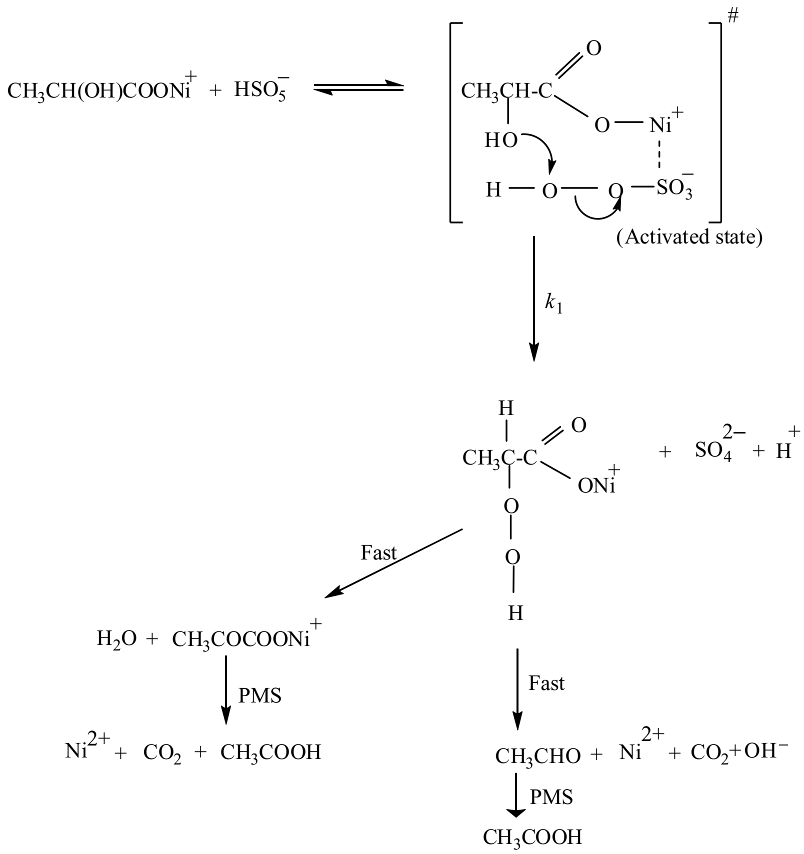

Figure 3 A mechanistic scheme for the reaction with HSO_5^-.

the two ions of opposite charge. Thus the observed entropy of activation shows that the oxidation of nickel lactate by HSO_5^- may proceed through intermolecular interaction and is shown in Fig. 3.

It has been shown that the oxidation of glycolic acid by PMS in the presence of Ni(II) and Cu(II) proceeds through the formation of hydroperoxide intermediate [3]. When the reactions are carried out in the presence of formaldehyde and [HCHO] > [Ni(II)], the rate is second order with respect to [PMS] and we observed the decomposition of PMS instead of the oxidation of nickel lactate [17]. Similar change in the mechanism is also observed in the nickel glycolate + HCHO + PMS system. This may be due to the formation of low molecular weight hemiacetals [18] as in Eq. (13).

$$CH_3CH(OH)COONi^+ + HCHO \rightleftharpoons HOCH_2OCH(CH_3)COONi^+ \quad (13)$$

Thus hemiacetal formation may protect the α-hydroxy group, and this may the reason for the change in the mechanism. Therefore, the oxidation of glycolate and lactate, in the presence of Ni(II), proceeds through the same active center, namely the alpha hydroxyl group.

We can compare the relative reactivity of HSO_5^- and SO_5^{2-} toward nickel lactate. Substituting the literature value of K_d in $k_2K_dK_3$ ($=k_2K_2$), we get k_2K_3 is 4.03×10^3 M^{-1} s^{-1} at 25°C and this can be compared with k_1 values given in Table I. Perusal shows that the ionized form of the oxidant (SO_5^{2-}) is more reactive by approximately four orders of magnitude. This may be due to the different reaction of HSO_5^- and SO_5^{2-} with metal ion M^+ [14,15] as discussed earlier. Thus SO_5^{2-} may form an ion pair with nickel ion of nickel lactate, and this may be the reason for the intramolecular oxidation–reduction mechanism (Fig. 4).

The large difference in the rate constants can also explain why we could not observe the reaction between HSO_5^- and nickel glycolate. According to the reactivity-selectivity principle [19–21], the more reactive oxidant/substrate should be less selective than the lower reactive one. Because SO_5^{2-} is $\sim10^4$ times more reactive, it should be less selective and hence less susceptible to the substituent effect. This will explain why the k_2K_2 values of nickel lactate are slightly higher than nickel glycolate (Table I). The influence of the

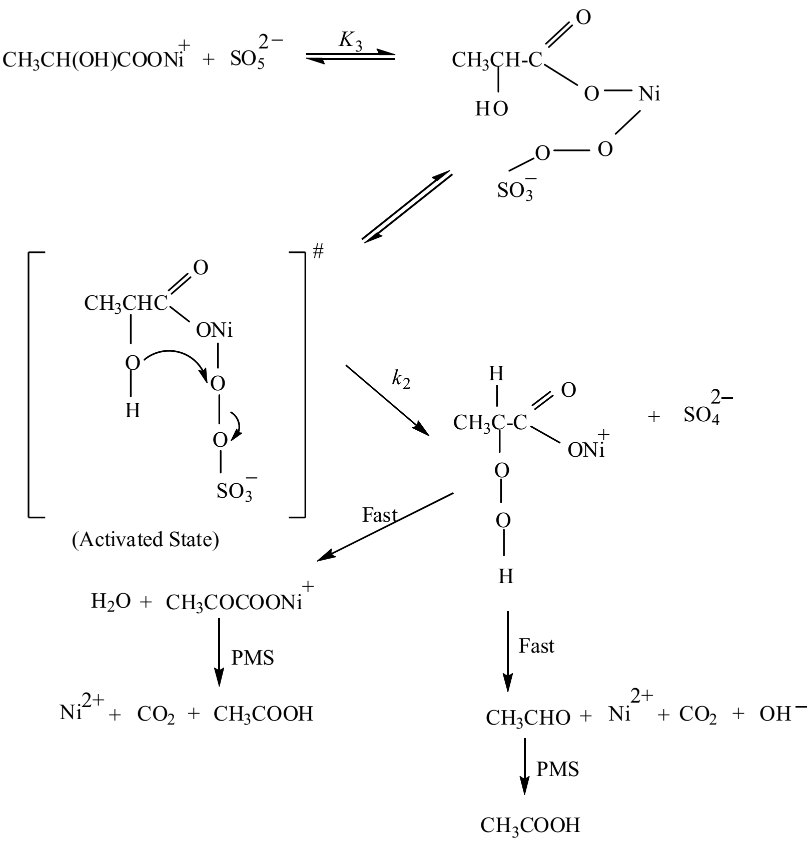

Figure 4 A mechanistic scheme for the reaction with SO_5^{2-}.

substituent may be more effective with the less reactive HSO_5^-, and this may be the reason that we could not observe k_1 values in nickel glycolate–PMS system.

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