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## MICELLAR EFFECT ON CHROMIUM(VI) OXIDATION OF ETHANOL AND PROPAN-1-OL IN AQUEOUS ACID MEDIA

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### Abstract

Cetylpyridinium chloride (CPC) inhibits the Cr(VI) oxidation of ethanol and propan-1-ol while sodium dodecyl sulfate (SDS) catalyzes the title reactions. At higher values of the [surfactant], the rate attains a limiting value. The micellar effect has been explained by considering the preferential partitioning of the reactants in terms of the suggested mechanism. Applicability of the Menger-Portnoy model and Piskiewicz model to explain the observed micellar effect has been examined.

*Keywords* : Kinetics, micelles, Cr(VI), alkanols

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### INTRODUCTION

Studies of reaction mechanism in organized assemblies are important from the standpoint that many biochemical reactions proceed in a microheterogeneous system, which contains an aqueous and a lipophilic moiety. Among the biochemical reactions, electron transfer is of primary importance. The electron transfer reactions in micellar systems can be regarded as models to get an insight into the electron transfer reactions occurring in biological systems. Effect of such organized structures on the electron transfer reactions has already earned considerable attention [1]. Alcohol oxidation is a very important kind of chemical reaction and Cr(VI) is one of the most important oxidants for organic substrates. Recently, it has been found [2] that the micelles can significantly influence the kinetics and mechanistic aspects of Cr(VI) oxidation of different organic substrates and the observed micellar effect can strongly substantiate the proposed reaction mechanism. Thus the title investigation appears worth exploring.

## EXPERIMENTAL

The alcohols (RCH<sub>2</sub>OH) (E. Merck) were purified by refluxing with excess of freshly burnt quicklime, followed by distillation and the purity was checked by density measurement. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (BDH, AR), cetylpyridinium chloride, CPC (SRL), sodium dodecyl sulfate, SDS (SRL) and all other chemicals used were of highest purity available commercially. Under the kinetic conditions, [RCH<sub>2</sub>OH]<sub>T</sub> >> [Cr(VI)]<sub>T</sub>, the alcohols were quantitatively oxidized to the respective carbonyl compounds, which were identified by the preparation of their 2,4-DNP derivatives (yield ≈ 85-90%). This slightly decreased yield is probably due to the formation of hemiacetal between the carbonyl compound and the corresponding unreacted RCH<sub>2</sub>OH. No positive test [3] for the carboxylic acids due to further oxidation of the respective aldehydes was noticed. It indicates no further oxidation of the aldehydes under the experimental conditions. In the presence of excess RCH<sub>2</sub>OH, oxidation of the product is kinetically insignificant. To circumvent the solubility problem, effect of CPC was followed only in aqueous H<sub>2</sub>SO<sub>4</sub> media. Progress of the reaction was followed by quenching titrimetric technique as discussed earlier [2b]. The pseudo-first-order rate constants (*k*<sub>obs</sub>) were determined as usual from the rate of disappearance of Cr(VI). The *k*<sub>obs</sub> values were reproducible within the experimental error limit. Except the pseudo-first-order rate constants (*k*<sub>obs</sub>) all other kinetic parameters were estimated by using the least-squares method.

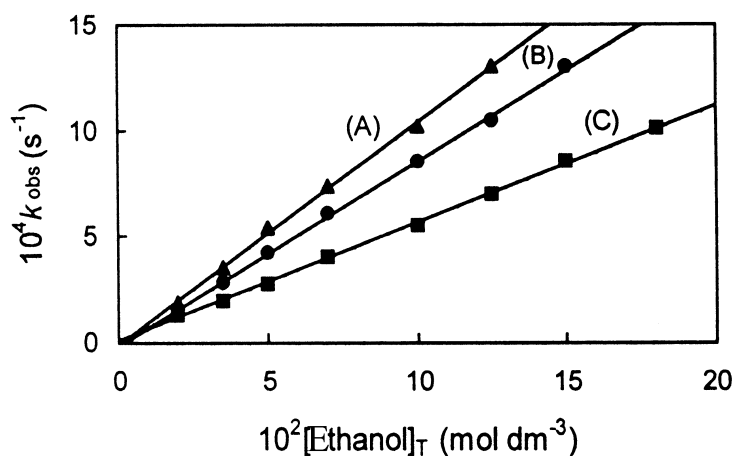
## RESULTS AND DISCUSSION

Under the kinetic condition, [RCH<sub>2</sub>OH]<sub>T</sub> >> [Cr(VI)]<sub>T</sub>, the rate of disappearance of Cr(VI) shows a first-order dependence on [Cr(VI)] both in the absence and presence of surfactants. The dependence on [RCH<sub>2</sub>OH]<sub>T</sub> is as follows :

$$-d\ln[\text{Cr(VI)}]/dt = k_{\text{obs}} = k_s[\text{RCH}_2\text{OH}]_T \quad (1)$$

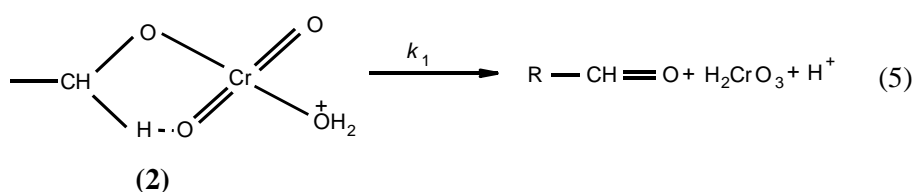
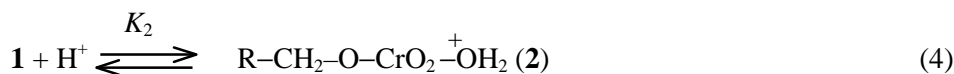
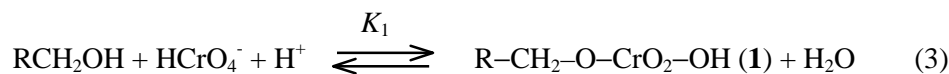
The specific rate constants (*k*<sub>s</sub>) in the presence and absence of surfactants, SDS and CPC have been estimated (*cf.* Fig. 1 and Table 1) from the plots of *k*<sub>obs</sub> *vs.* [substrate]<sub>T</sub> (*r* ≥ 0.98). They indicate that CPC inhibits the reaction, while SDS catalyzes the reaction. The H<sup>+</sup> dependence in aqueous HClO<sub>4</sub> was followed both in the presence and absence of SDS and the observed rate law at fixed [RCH<sub>2</sub>OH]<sub>T</sub> is :

$$k_{\text{obs}} = k_H[\text{H}^+]^2 \quad (2)$$



**Fig. 1.** Effect of  $[\text{ethanol}]_T$  on  $k_{\text{obs}}$  for the Cr(VI) oxidation of ethanol in aqueous  $\text{H}_2\text{SO}_4$  media in the presence and absence of surfactants (SDS and CPC).  $[\text{Cr(VI)}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ ;  $32^\circ\text{C}$ . A ( $[\text{SDS}]_T = 0.025 \text{ mol dm}^{-3}$ ); B (without any surfactant); C ( $[\text{CPC}]_T = 5 \times 10^{-3} \text{ mol dm}^{-3}$ )

The values of  $k_H$  were estimated (*cf.* Table 1 and Fig. 2) from the plots of  $k_{\text{obs}}/[\text{H}^+]$  vs.  $[\text{H}^+]$  ( $r \geq 0.98$ ). The following ester formation mechanism [4] conforms to the observed rate law.



**Scheme 1.** Cr(VI) oxidation of ethanol ( $\text{R} = \text{CH}_3$ ) and propan-1-ol ( $\text{R} = \text{C}_2\text{H}_5$ )

In the proposed cyclic transition state (2), the redox decomposition occurs through hydride/hydrogen ion transfer [5]. In this electrocyclic process, a Hückel-type molecular orbital (consisting of 6 electrons) involving the  $t_{2g}$

orbital of Cr-centre is produced. The protonation on Cr–O bond (*cf.* eq. 4) facilitates electron flow towards Cr(VI) to produce Cr(IV). Cr(IV) then participates in the subsequent faster reactions in different possible ways [6]. In terms of Rocek mechanism [6a], Cr(IV) reacts with RCH<sub>2</sub>OH to form Cr(III) and the free radical RC<sup>•</sup>HOH (which initiates polymerization of acrylonitrile and this radical is ultimately oxidized to RCHO by Cr(VI)) and in terms of Perez-Benito mechanism [6b], Cr(IV) reacts with RCH<sub>2</sub>OH through hydride transfer (*i.e.* 2e transfer step) to form Cr(II) (which is rapidly oxidized by Cr(VI) to Cr(III)) and RCHO through the generation of an intermediate carbocation center which is responsible for acrylonitrile polymerization. The equilibrium constants  $K_1$  and  $K_2$  are quite low. By considering the stoichiometry of the reaction, Scheme I leads to :

$$k_{\text{obs}} = (2/3)K_1K_2k_1[\text{RCH}_2\text{OH}]_{\text{T}}[\text{H}^+]^2 \quad (6)$$

Equation 6 conforms to the experimental findings.

**Table 1**

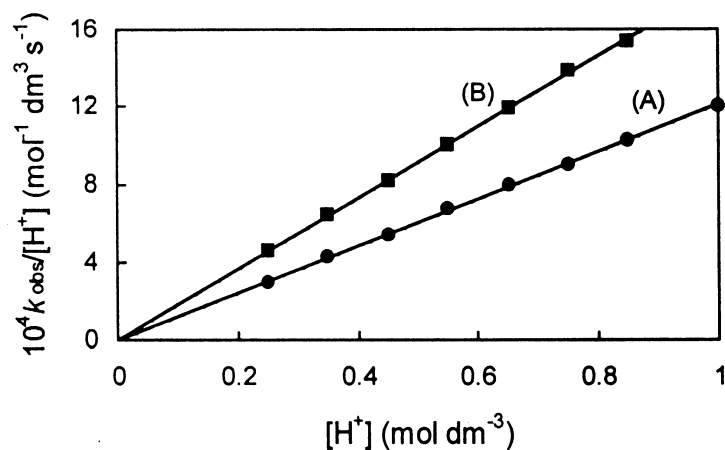
Kinetic parameters (at 32°C) for the Cr(VI) oxidation of ethanol and propan-1-ol in aqueous acidic media. [Cr(VI)] =  $2 \times 10^{-3}$  mol dm<sup>-3</sup>; For  $k_s$ : [H<sub>2</sub>SO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup>;  $10^3[\text{CPC}]_{\text{T}} = 5.0$  (for ethanol), = 2.0 (for propan-1-ol); [SDS]<sub>T</sub> = 0.025 mol dm<sup>-3</sup> (for ethanol), = 0.04 mol dm<sup>-3</sup> (for propan-1-ol). For  $k_{\text{H}}$ : [RCH<sub>2</sub>OH]<sub>T</sub> = 0.05 mol dm<sup>-3</sup>, [SDS]<sub>T</sub> = 0.02 mol dm<sup>-3</sup>, I = 1.5 mol dm<sup>-3</sup>. W, CPC and SDS indicate the respective rate constants in the absence of any surfactant, in the presence of CPC and in the presence of SDS respectively

RCH <sub>2</sub> OH	$10^3 k_s / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			$10^4 k_{\text{H}} / \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	
	W	CPC	SDS	W	SDS
Ethanol	$8.6 \pm 0.1$	$5.7 \pm 0.1$	$10.4 \pm 0.2$	$9.2 \pm 0.2$	$11.5 \pm 0.2$
Propan-1-ol*	$10.4 \pm 0.2$	$8.0 \pm 0.1$	$12.1 \pm 0.2$	$12.1 \pm 0.2$	$18.4 \pm 0.3$

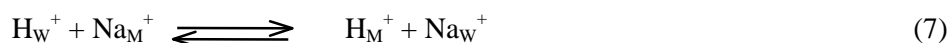
\* values of  $k_s$  are at 35°C

From the effect of [surfactant]<sub>T</sub> on  $k_{\text{obs}}$ , it is found (*cf.* Fig. 3) that CPC inhibits the reaction continuously and it attains a limiting value at high [CPC]<sub>T</sub>. On the other hand, SDS accelerates the rate process and  $k_{\text{obs}}$  value is ultimately saturated. The observed micellar effect can be explained by considering the partitioning behavior of the reactants between the micellar and aqueous phases. The neutral alkanols are likely to be preferably distributed in the micellar phase and the kinetically active H<sub>2</sub>CrO<sub>4</sub> species [7] may remain concentrated in the Stern layer of micellar phase [8]. This leads to generation of Cr(VI)-alkanol ester in the micellar interphase. The Cr(VI)-ester (1) is neutral and it is

concentrated in the Stern layer of micellar phase (the alkyl groups of **1** are projected towards the hydrophobic core). For the redox decomposition of the ester, it needs protonation (*cf.* eq. 4) which facilitates the electron flow towards Cr(VI). The approach of  $H^+$  towards the micellar phase where the ester is concentrated is disfavored for CPC due to the electrostatic repulsion by the positive micellar head groups, while the approach of  $H^+$  towards the micellar phase of SDS (anionic surfactant) is favored due to the electrostatic attraction through the following ion exchange equilibrium.

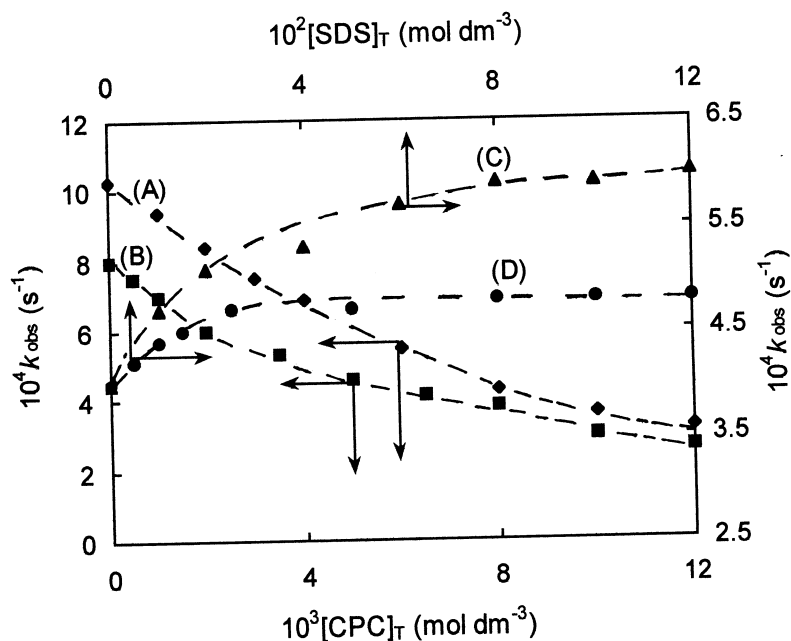


**Fig. 2.** Effect of  $[H^+]$  on  $k_{obs}$  for the Cr(VI) oxidation of propan-1-ol in aqueous  $HClO_4$  media in the presence and absence of SDS.  $[Cr(VI)]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[propan-1-ol]_T = 0.05 \text{ mol dm}^{-3}$ ;  $I = 1.5 \text{ mol dm}^{-3}$ ,  $32^\circ C$ ; A (without any surfactant); B ( $[SDS]_T = 0.02 \text{ mol dm}^{-3}$ )



Here, the subscripts W and M denote the aqueous phase and micellar phase respectively. Thus, CPC restricts the reaction only in aqueous phase where the concentration of the species (**1**) is significantly decreased due to the preferential partitioning of the ester (**1**) into the micellar phase. It explains the rate retardation by CPC. On the other hand, in the presence of SDS, the reaction goes on simultaneously in both aqueous phase and micellar phase with an enhanced rate in the micellar phase due to the preferential accumulation of the ester (**1**) and  $H^+$  in the micellar phase. With the increase of  $[SDS]_T$ , the amount of solubilized reactants in the micellar phase increases but at the same time the increased  $[SDS]_T$  exerts a dilution effect. Besides this, with the increase of

$[\text{SDS}]_{\text{T}}$ , the concentration of counterion (*i.e.*  $\text{Na}^+$ ) also increases to drive the equilibrium 7 to the left direction. Because of these opposing factors, the rate gets saturated at higher  $[\text{SDS}]_{\text{T}}$ .



**Fig. 3.** Effect of  $[\text{surfactant}]_{\text{T}}$  (A, B for CPC; C, D for SDS) on  $k_{\text{obs}}$  for the Cr(VI) oxidation for ethanol and propan-1-ol in aqueous  $\text{H}_2\text{SO}_4$  media.  $[\text{Cr(VI)}]_{\text{T}} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ . A ( $[\text{C}_2\text{H}_5\text{OH}]_{\text{T}} = 0.1 \text{ mol dm}^{-3}$ ,  $35^\circ\text{C}$ ); B ( $[\text{C}_3\text{H}_7\text{OH}]_{\text{T}} = 0.105 \text{ mol dm}^{-3}$ ,  $30^\circ\text{C}$ ); C ( $[\text{C}_3\text{H}_7\text{OH}]_{\text{T}} = 0.04 \text{ mol dm}^{-3}$ ,  $35^\circ\text{C}$ ); D ( $[\text{C}_2\text{H}_5\text{OH}]_{\text{T}} = 0.03 \text{ mol dm}^{-3}$ ,  $40^\circ\text{C}$ )

By considering the pseudo-phase kinetic model proposed by Menger and Portnoy [9], it gives the following rate law :

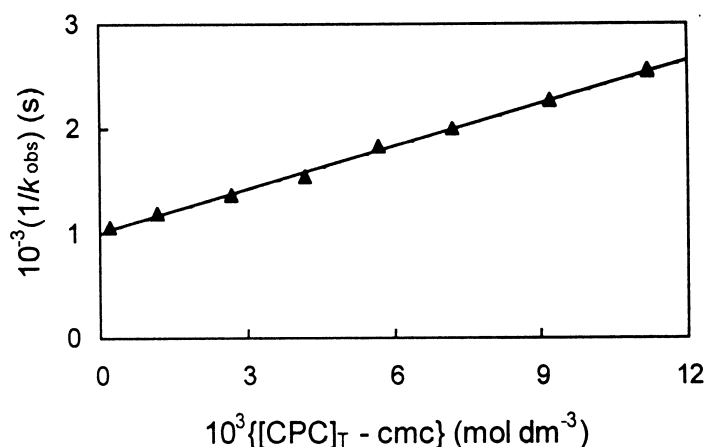
$$1/(k_{\text{W}} - k_{\text{obs}}) = 1/(k_{\text{W}} - k_{\text{m}}) + (N/K_{\text{B}}) \{1/[\text{D}_n]\} \{1/(k_{\text{W}} - k_{\text{m}})\} \quad (8)$$

where,  $[\text{D}_n] = ([\text{surfactant}]_{\text{T}} - \text{cmc})/N$ ,  $\text{cmc}$  = critical micelle concentration,  $N$  = aggregation number;  $k_{\text{W}}$  and  $k_{\text{m}}$  are the first-order rate constants in aqueous and micellar phase respectively and include the concentration of the other reactant

in these pseudo-phases;  $K_B$  = binding constant of the partitioned reactant. Taking  $\text{cmc} = 8 \times 10^{-4} \text{ mol dm}^{-3}$  [10], the linearity of the plot of  $1/(k_W - k_{\text{obs}})$  vs.  $1/[D_n]$  (not shown) has been verified for the CPC inhibited reaction and it leads to  $k_m \approx 0$  and  $\log(K_B/N) \approx 2.2$  at  $35^\circ\text{C}$  in  $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  for the title alcohols. Taking  $k_m \approx 0$ , eq. 8 reduces to eq. 9.

$$1/k_{\text{obs}} = 1/k_W + (K_B/N) (D_n/k_W) \quad (9)$$

The linearity of the plot of  $1/k_{\text{obs}}$  vs.  $[D_n]$  (Fig. 4) has been verified and the estimated  $k_W$  value nicely conforms to the experimental value. Thus the estimated  $K_B/N$  values are also in good agreement with those obtained by using eq. 8.



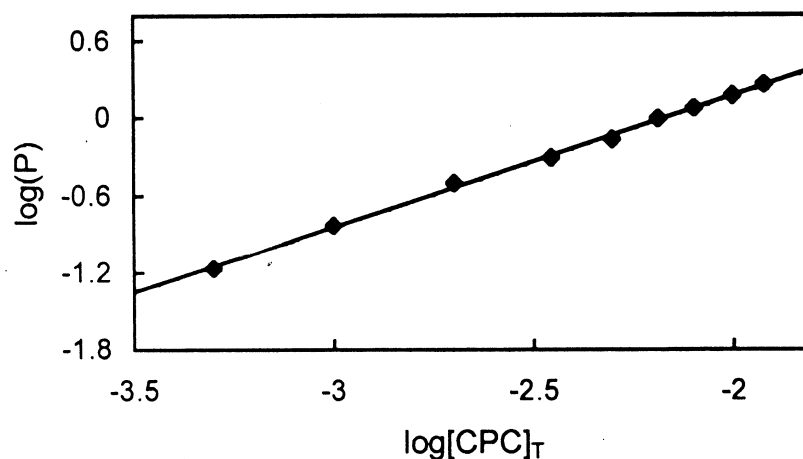
**Fig. 4.** The plot of  $1/k_{\text{obs}}$  vs.  $([\text{CPC}]_T - \text{cmc})$  to explain the micellar effect on  $k_{\text{obs}}$  for the Cr(VI) oxidation of propan-1-ol in aqueous  $\text{H}_2\text{SO}_4$  media.  $[\text{Cr(VI)}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ ;  $[\text{propan-1-ol}]_T = 0.105 \text{ mol dm}^{-3}$ ;  $35^\circ\text{C}$

The rate data in the presence of CPC was subjected to Piszkiwicz model [11] which relates cooperativity between the neutral reactant and surfactant to aggregate to form the reactive micelle and its contribution to the rate is given by:

$$\log[(k_{\text{obs}} - k_W)/(k_m - k_{\text{obs}})] = \log(P) = n \log[\text{CPC}]_T - \log K_D \quad (10)$$

where  $K_D$  is the dissociation constant of micellized surfactant back to its component;  $n$  is the index of cooperativity. Equation 10 needs no knowledge of

cmc, which is not very often available under the kinetic conditions. Though eq. 10 was originally developed for the micelle catalyzed reactions showing a maximum rate followed by inhibition, the model has been applied by different workers [12] to explain the micellar effect in which the reaction is inhibited or catalyzed by the micelles over the whole range as observed in the present system. The plot of  $\log(P)$  vs.  $\log[\text{CPC}]_T$  (cf. Fig. 5) (taking  $k_m = 0$ ) leads to the values :  $n = 1-1.3$ ,  $-\log K_D \approx 2.2-2.7$ . The estimated  $\log[\text{CPC}]_{50}$  (which represents concentration of the surfactant required for half-maximal catalysis or inhibition) values nicely agree with those experimentally found. The values of  $n \approx 1$ , far less than the aggregation number (20 to 100) (ref. 11) of the surfactant molecules leading to micelles indicate the existence of catalytically productive submicellar aggregates. From the  $\log K_D$  values, it is evident that the interaction between the reactant and surfactant is fairly high.



**Fig. 5.** Applicability of Piskiewicz model (*i.e.* plot of  $\log(P)$  vs.  $\log[\text{CPC}]_T$ ) to explain the micellar effect on  $k_{\text{obs}}$  for the Cr(VI) oxidation of propan-1-ol in aqueous  $\text{H}_2\text{SO}_4$  media.  $[\text{Cr(VI)}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$ ;  $[\text{propan-1-ol}]_T = 0.105 \text{ mol dm}^{-3}$ ;  $35^\circ\text{C}$ .  $P$  is defined as :  $P = (k_w - k_{\text{obs}})/(k_{\text{obs}} - k_m)$

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