

Kinetics of Oxidation of Aliphatic Alcohols by Potassium Dichromate in Aqueous and Micellar Media

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ABSTRACT

The kinetics of oxidation of four aliphatic alcohols in acidic aqueous and micellar media were investigated. The reaction was found to be first-order with respect to both alcohol and oxidant. Pseudo-first-order kinetics were found to be perfectly applicable with ethanol, 1-propanol and 2-propanol while deviation was observed at intermediate stages of the reaction with methanol. The pseudo-first-order rate constants were found to be independent of concentration of the oxidant. The presence of TX-100 enhanced the rate of the reaction for all alcohols. Negative salt effects were observed with addition of KCl to the reaction mixture. A suitable mechanism for the reaction was suggested which agrees with the experimental findings.

KEYWORDS

Oxidation, dichromate, alcohol, pseudo-first-order, micellar effect.

1. Introduction

Oxidation of alcohols has been studied extensively using different oxidizing agents and in various media.^{1–7} One of the most commonly used oxidants is dichromate and its derivatives. In going through the literature, one finds controversial results regarding the kinetics of these reactions though all studies have proposed similar mechanisms. Some reports suggested applicability of pseudo-first-order kinetics with Michaelis-Menten kinetics.^{1,2} Other studies showed that while long chain alcohols follow pseudo-first-order kinetics, short chain alcohols fit to a two-exponential equation.³ Others reported that the reaction is first-order in both substrate and oxidant.⁴ The reaction has, however, not been studied in surfactant media to examine the micellar effect on the reaction rate. This has motivated us to investigate the oxidation of some aliphatic alcohols and try to resolve some of these issues. This paper reports the kinetics of oxidation of alcohols, namely, methanol, ethanol, 1-propanol and 2-propanol, in aqueous as well as in micellar media by using potassium dichromate as oxidant. Potassium dichromate was reported to oxidize primary alcohols to the corresponding aldehydes which in turn are oxidized to carboxylic acids.⁸ We expect that when the concentration of alcohol is much greater than that of the oxidant further oxidation of the aldehyde to the carboxylic acid will be stopped. This requirement will also achieve pseudo-first-order conditions.

2. Experimental

2.1. Materials

All alcohols, sulfuric acid, hydrochloric acid, potassium dichromate and potassium chloride were of analytical grade and purchased from Fisher Scientific, UK. TX-100 (polyoxyethylene p-t-octylphenol) was of general grade and obtained from Avonchem, UK. All chemicals were used as received without further purification. Stock solutions of sulfuric acid (4 mol dm⁻³) and potassium dichromate (0.02 mol dm⁻³) were prepared in double-distilled water and kept in the dark until needed.

2.2. Kinetic Measurements

A volume of 50 mL of sulfuric acid and 5 mL of potassium dichromate was transferred to a 250 mL conical flask and kept in a thermostated water bath along with a separate vessel that contained the required amount of alcohol. After thermal equilibrium was reached, the alcohol was added to the sulfuric acid–potassium dichromate mixture with gentle stirring and the absorbance of reaction mixture was measured at specific time intervals. The absorbance was read at 440 nm with a UV/Vis-2100 spectrophotometer. The concentration of alcohol was varied over the range 0.05–0.12 mol dm⁻³ (25-fold excess) which ensures pseudo-first-order conditions. To study the temperature-dependence of the reaction, the reaction temperature was varied between 15 and 31 °C. The micellar and salt effects were examined by running separate experiments in the presence of 0.01 mol dm⁻³ TX-100 while varying the concentration of KCl and keeping all other conditions fixed.

2.3. Product Analysis and Stoichiometry

An aliquot of 40 mL of the reaction mixture was used after reaction completion for product detection and analysis. This solution was treated with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ hydrochloric acid and kept overnight under refrigeration.¹ Yellow precipitates formed which were filtered, washed, recrystallized from ethanol and dried. The melting points of the precipitates were found to match those of 2,4-dinitrophenylhydrazones (DNPs) of aldehydes. The yields of the DNPs were in the range 50.8–73.7 %. The oxidation of alcohols by potassium dichromate to give the corresponding aldehydes can be represented by the following stoichiometry:



3. Results and Discussion

Figure 1 shows plots of $\ln(A_0/A_t)$ versus time at 297 K. The plots for ethanol, 1-propanol and 2-propanol gave excellent fits to straight lines ($r > 0.99$) while that for methanol deviated from

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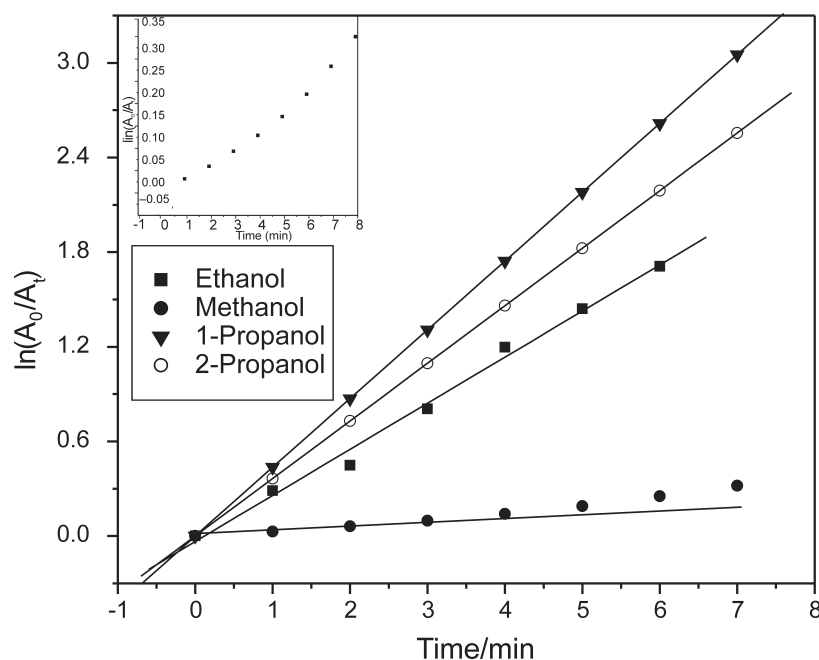


Figure 1 Plots of $\ln(A_0/A_t)$ vs. time at the following conditions: $[H_2SO_4] = 4 \text{ mol dm}^{-3}$; $[\text{alcohol}] = 0.07 \text{ mol dm}^{-3}$; $[K_2Cr_2O_7] = 0.0018 \text{ mol dm}^{-3}$; 297 K. The inset shows the deviation from linearity exhibited by methanol.

Table 1 Values of k_{obs} obtained for different concentrations of the alcohols and the following fixed conditions: $[K_2Cr_2O_7] = 1.8 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 4 \text{ mol dm}^{-3}$; 297 K.

Concentration/mol dm^{-3}	$k_{\text{obs}}/\text{min}^{-1}$			
	Ethanol	Methanol	1-Propanol	2-Propanol
0.05	0.193	0.011	0.288	0.264
0.07	0.292	0.015	0.436	0.365
0.09	0.425	0.025	0.582	0.457
0.12	0.598	0.029	0.832	0.606
0.07 (with TX-100)	0.353	0.061	0.511	0.524
$k_2 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ at 297 K	5.781	0.270	7.759	4.863

linearity at 30–40 % of reaction completion. Beniso and Rodenas³ have observed this behaviour with methanol and ethanol when oxidized with dichromate in $HClO_4$ medium and explained this behaviour by a mechanism which involves an intermediate reaction between chromic acid and $HClO_4$. In this study, in which the solvent is H_2SO_4 , deviation from linearity was observed only with methanol.

The observed rate constants, k_{obs} , were calculated from the slopes of the straight lines by linear regression. For methanol, the slopes were calculated for the straight lines which were fitted to the data taken at the early stages of the reaction. These values obtained for different concentrations of the alcohols and for a fixed concentration of dichromate are presented in Table 1. The order of reactivity of the alcohols is as follows:

1-Propanol > 2-Propanol > Ethanol > Methanol.

It appears that the reactivity increases with the alcohol chain length. The slightly higher rate constant of 1-propanol over that of 2-propanol may be attributed to steric hindrance of the two methyl groups attached to carbonyl group in the case of the latter.

3.1. Effect of Variation of Alcohol Concentration

The observed rate constants k_{obs} were plotted against concentrations of alcohols in Fig. 2.

The plots were fitted successfully ($r > 0.995$) to straight lines indicating that the order of the reaction with respect to alcohol is unity. To confirm this result, the logarithms of the rate constants were plotted against the logarithms of alcohol concentrations. The plots were also linear with slopes close to unity. Hence, the general rate equation of the reaction can be written as:

$$R = k_2[\text{Alcohol}][\text{Dichromate}], \quad (2)$$

where k_2 is the second-order rate constant, the values of which at 297 K are shown in Table 1.

3.2. Effect of Concentration of the Oxidant

The values of k_{obs} for ethanol at 297 K at different concentrations of dichromate and fixed alcohol concentration (0.09 mol dm^{-3}) are presented in Table 2. These values are the same within 4 % of error which indicates that there is no effect of the concentration of the oxidant on the observed rate constant. A negative effect with increasing concentration of Cr^{IV} was observed during the oxidation of DL-methionine and (S)-phenylmercaptoacetic acid.^{9,10} The explanation which was given is that variation of dichromate concentration leads to a change in the protonated chromate ion concentration which is believed to be the effective oxidant. This effect was not observed in this work and other related works,^{11,12} and leads us to believe that solvent plays a decisive role in this regard.

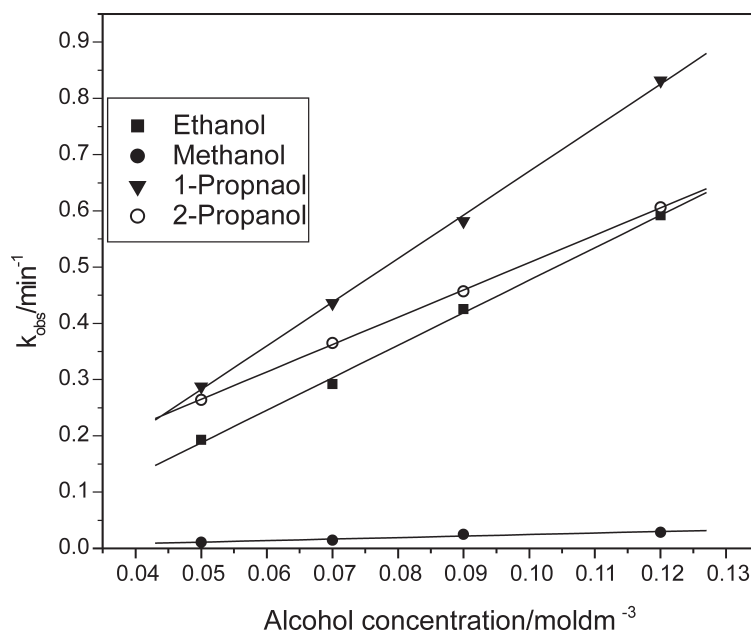


Figure 2 Plots of k_{obs} vs. concentration of alcohols at the following conditions: $[\text{H}_2\text{SO}_4] = 4 \text{ mol dm}^{-3}$; $[\text{K}_2\text{Cr}_2\text{O}_7] = 0.0018 \text{ mol dm}^{-3}$; 297 K.

Table 2 Values of the observed rate constant at varying concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$, KCl and H_2SO_4 .

[ethanol]/mol dm ⁻³	$10^3[\text{Cr}^{\text{VI}}]/\text{mol dm}^{-3}$	$[\text{H}_2\text{SO}_4]/\text{mol dm}^{-3}$	[KCl]/mol dm ⁻³	$k_{\text{obs}}/\text{min}^{-1}$
0.09	1.3	4.0	0	0.397
0.09	1.8	4.0	0	0.413
0.09	2.5	4.0	0	0.404
0.09	1.8	2.0	0	0.051
0.09	1.8	3.0	0	0.087
0.09	1.8	4.0	0	0.413
0.09	1.8	4.0	0.05	0.174
0.09	1.8	4.0	0.10	0.141

3.3. Effect of Solvent

The values of k_{obs} for ethanol oxidation at 297 K at various concentrations of sulfuric acid and fixed concentrations of alcohol and oxidant are shown in Table 2. As the concentration of sulfuric acid decreased, the observed rate constant decreased remarkably.

3.4. Micellar Effect

The values of k_{obs} for alcohol oxidation reactions which were performed in presence of TX-100, a non-ionic surfactant, at 297 K are presented in Table 1. The rate constants for all alcohols were enhanced. Micellar catalysis with non-ionic micelles was observed to occur because of the binding of the substrates onto the micellar surface by hydrophobic and/or electrostatic interaction. This binding increases the encounter probability, leading to an accelerated rate of reaction.¹³ The catalytic effect of micellar media was also observed by other researchers.^{14,15}

3.5. Effect of Salt Concentration

The values of k_{obs} for ethanol oxidation reactions in the presence of varying concentrations of KCl are shown in Table 2. The rate constant decreased by more than 100 % with addition of 0.05 mol dm^{-3} KCl and this decrease continued with further additions of the salt but with lower rate. The negative salt effect indicates that the rate-determining step of the reaction occurs between reactants of opposite charges.¹⁶

3.6. Temperature Dependence

Linear plots ($r > 0.99$) resulted when $\log(k_{\text{obs}})$ vs. $1/T$ (Figure 3) were depicted. Activation energies of the reactions were calculated from the slopes of the lines and are shown in Table 3, along with other kinetic parameters ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger . Negative transition entropies indicate an associative transition state. The comparable values of ΔG^\ddagger indicate that a similar mechanism is operative for the oxidation of all four alcohols.¹⁷

4. Mechanism

Based on our experimental results, the most appropriate mechanism for the reaction is depicted in Scheme 1, where the protonated alcohol approaches the chromate anion resulting in formation of an intermediate complex that is called chromate ester. This complex dissociates in the rate-determining step to give the aldehyde and Cr^{IV} . Cr^{IV} is involved in further reaction with Cr^{VI} to give Cr^{V} that is reduced by another molecule of alcohol to finally give Cr^{III} .

5. Conclusion

The oxidation of alcohols by potassium dichromate in H_2SO_4 medium has been verified to follow pseudo-first-order rate kinetics with the exception of methanol which started to deviate at an intermediate stage of the reaction. In general, we can state that the reaction is first-order with respect to both alcohol and dichromate. The pseudo-first-order rate constants were found

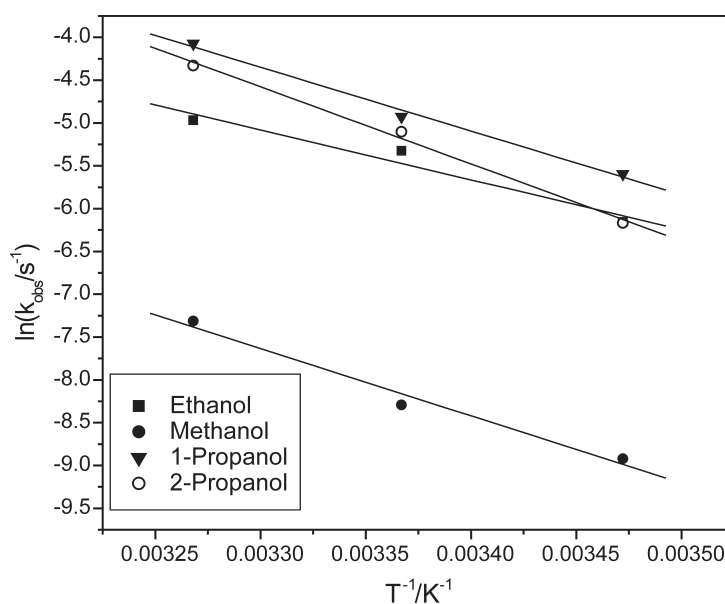
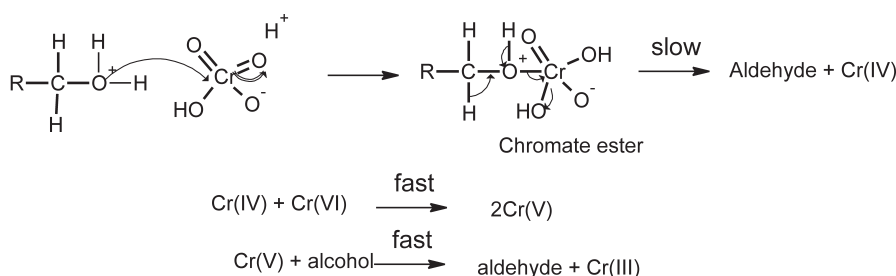


Figure 3 Plots of $\ln k_{\text{obs}}$ vs. $1/T$ at the following conditions: $[\text{H}_2\text{SO}_4] = 4 \text{ mol dm}^{-3}$; $[\text{alcohol}] = 0.07 \text{ mol dm}^{-3}$; $[\text{K}_2\text{Cr}_2\text{O}_7] = 0.0018 \text{ mol dm}^{-3}$

Table 3 Kinetic parameters for the reaction calculated at the following conditions: $[\text{alcohol}] = 0.09 \text{ mol dm}^{-3}$; $[\text{Cr}^{\text{VI}}] = 0.0018 \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 4 \text{ mol dm}^{-3}$; 297 K.

Alcohol	$E_a/\text{kJ mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1}\text{mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
Ethanol	48.460	45.990	-126.472	83.552
Methanol	65.358	62.888	-92.203	90.273
1-Propanol	61.400	59.930	-76.234	84.041
2-Propanol	74.598	72.128	-35.584	82.696



Scheme 1

to be independent of oxidant concentration. The rate of the reaction was enhanced in the presence of surfactant and diminished with addition of salts. The proposed mechanism involves the chromate ion and protonated alcohol as reactants with chromate ester as an intermediate complex.

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