



### Kinetics Of Oxidation Of Allyl Alcohol By Diorthotelluraocuprate(III) Complex Ion In Alkaline Medium


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**ABSTRACT**

The kinetics of oxidation of allyl alcohol(AA) by diorthotelluraocuprate(III) complex ion(DTC) was studied spectrophotometrically in alkaline medium in a temperature range of 25–30°C. The results show that the reaction is first order with respect to DTC, the observed reaction order is 3.321 ~ 3.502 for AA, which is much greater than the reported value. It is found that the pseudo first order ( $[AA] \gg [DTC]$ ) rate constant  $k_{obs}$  increases with the increase in  $[OH^-]$  and decreases with the increase in  $[TeO_4^{2-}]$ . A weak negative ionic strength effect was observed. Under the protection of nitrogen, the reaction system can induce polymerization of acrylamide, which shows that the reaction involves free radical.

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**KEYWORDS**

$XeO_3F_2$ ;  
 Mean amplitudes of  
 vibration;  
 Bond properties.

**INTRODUCTION**

Allyl alcohol(AA) is an important intermediate in medical products, pesticide and spice. Its derivants can be used to synthesize chloroepoxy propane, glycerol, 1,4-butylene glycol, allylacetone etc, also can be as an important material for plasticizing agent and engineering plastics. Moreover its carbonate is an im-

portant material for optical resin, safety glass and display screen etc. Up to now, the kinetics of oxidation of AA has been reported<sup>[1]</sup>, different oxidants were used in the reactions such as potassium permanganate, chromic acid, vanadium(V), manganese pyrophosphate, silver(III), chloramine-T, etc. But all the reactions are very slow in acid or alkaline medium, and the observed reaction order is less than 1 for AA.

In general, transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands. In recent years, the study on the complex of transition metals in a high oxidation state has intrigued many researchers' interests, due to their strong oxidation and stability, which can provide new and valuable information in some fields. The kinetics of oxidation of organic by this kind of complex has been reported<sup>[2-7]</sup>, but the study on the oxidation of alcohol by diorthotelluraocuprate(III) complex ion(DTC) is few.

In our present work, the kinetics of oxidation of AA by DTC was studied for the first time. It is found that the observed reaction order with respects to AA is 3.21~3.502, which much higher than the reported value<sup>[1]</sup>.

## EXPERIMENTAL

### Reagents and instruments

Potassium persulphate ( $K_2S_2O_8$ ), copper sulphate ( $CuSO_4$ ), potassium tellurite ( $K_2TeO_3$ ), potassium nitrate ( $KNO_3$ ), sodium sulphate ( $Na_2SO_4$ ) were of A.R. grade. Doubly distilled water was employed throughout the experiment. Solutions of DTC and AA were always freshly prepared before use with stock solution and twice-distilled water. The Solution of DTC in a strong alkaline medium was prepared and standardized by the method of Chandra and Yadara<sup>[8]</sup>. In UV-Vis spectrum of as-prepared DTC, maximum absorption peak ( $\lambda=403nm$ ) was found to be consistent with the reported<sup>[9]</sup>.  $KNO_3$  and  $Na_2SO_4$  were used to adjust ionic strength ( $\mu$ ) of the solution.

UV-3000 spectrophotometer (Japan, Shimadzu) with 10mm thick glass cell was used to track the reaction, and TB-85 thermobath (Japan, Shimadzu) was used to control temperature( $\pm 0.1^\circ C$ ).

### Kinetic measurements

2mL solution containing definite [DTC],  $[TeO_4^{2-}]$ ,  $[OH^-]$  and ionic strength ( $\mu$ ) and 2mL AA solution of appropriate concentration were transferred separately to the upper and lower branch tubes of a  $\lambda$  type two-cell reactor. After it was thermally equilibrated at desired temperature in TB-85 thermobath,

two solutions were well mixed and immediately transferred to a 10mm thick glass cell, then put it in a constant temperature cell-holder. The reaction process was monitored automatically by recording the variation of absorbance (A) of the reaction mixture with time (t) at 403nm with a UV-3000 spectrometer. In order to obtain the condition of pseudo first order,  $[AA] \gg [DTC]$ . According to the variation of A of the reaction mixture with t kinetics information of the system can be obtained.

### Reaction product analysis and free radical detection

The product of oxidation of AA was detected to be propenal by its characteristic spot test<sup>[10]</sup>. Acrylamide solution was added to the reaction mixture under the protection of nitrogen gas, a lot of white deposition could be found, while acrylamide solution was added to twice-distilled water, no deposition could be found, which indicates that the reaction system can initiate polymerization of acrylamide and proves free radicals were generated in the reaction.

## RESULTS AND DISCUSSIONS

### Evaluation of pseudo-first-order rate constants $k_{obs}$

Under the condition of  $[AA] \gg [DTC]$ , the plot of  $\ln(A_t - A_\infty)$  versus t was linear, indicating that the reaction is first order with respect to DTC, where  $A_t$  and  $A_\infty$  were the absorbance at time t and at infinite time respectively. The pseudo-first-order rate constants ( $k_{obs}$ ), were evaluated by the method of least squares( $r > 0.999$ ). When [DTC] was changed,  $k_{obs}$  was a constant approximately (shown on TABLE 1).

We used generally 9~12  $A_t$  values within three times half life period to calculate  $k_{obs}$ .  $k_{obs}$  values were

TABLE 1: Effect of [DTC] on rate

[Cu(III)]/ mol·dm <sup>-3</sup>	$k_1/s^{-1}$	$k_2/s^{-1}$	$k_3/s^{-1}$	$k_{obs}/s^{-1}$
$5.475 \times 10^{-5}$	0.03139	0.03092	0.03170	0.03133
$2.738 \times 10^{-5}$	0.03106	0.03217	0.03135	0.03153

[AA] =  $5 \times 10^{-3} mol \cdot dm^{-3}$ ,  $[TeO_4^{2-}] = 5 \times 10^{-3} mol \cdot dm^{-3}$ ,  $[OH^-] = 0.1 mol \cdot dm^{-3}$ ,  $\mu = 0.125$ , T = 25°C

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at least averaged values of three independent experiments, reproducibility within  $\pm 5\%$  and general error less than  $\pm 8\%$ .

### Rate dependence on temperature and AA

As shown in TABLE 2, at fixed [DTC],  $[\text{TeO}_4^{2-}]$ ,  $[\text{OH}^-]$ , [AA] and  $m$ ,  $k_{\text{obs}}$  increased with the increase in temperature, and at fixed [DTC],  $[\text{TeO}_4^{2-}]$ ,  $[\text{OH}^-]$ ,  $m$  and temperature,  $k_{\text{obs}}$  increased drastically with the increase in [AA]. The plot of  $\ln k_{\text{obs}}$  versus  $\ln [\text{AA}]$  was a straight line ( $r > 0.99$ ). Evaluated from the slope, the observed reaction order ( $n_{\text{ap}}$ ) from  $k_{\text{obs}} = \frac{1}{2}K[\text{AA}]^{n_{\text{ap}}}$  was 3.321 and 3.502 with respect to [AA] respectively for 25°C and 30°C.

### Rate dependence on $[\text{OH}^-]$

**TABLE 2:  $k_{\text{obs}}$  in different temperature and different [AA]**

[AA] / mol·dm <sup>-3</sup>	10 <sup>3</sup> $k_{\text{obs}}$ / s <sup>-1</sup>	
	25°C	30°C
0.0075	1.960	2692
0.0150	21.82	22.04
0.0175	48.96	49.91
0.0200	75.96	78.04
0.0225	85.63	103.2
0.0250	122.9	130.9

[DTC] =  $5.475 \times 10^{-5}$  mol·dm<sup>-3</sup>,  $[\text{TeO}_4^{2-}] = 5 \times 10^{-3}$  mol·dm<sup>-3</sup>,  $[\text{OH}^-] = 0.1$  mol·dm<sup>-3</sup>,  $\mu = 0.125$

At fixed [DTC],  $[\text{TeO}_4^{2-}]$ , [AA], ionic strength ( $m$ ) and temperature,  $k_{\text{obs}}$  increased with the increase in  $[\text{OH}^-]$  (shown in TABLE 3), the plot of  $\ln k_{\text{obs}}$  vs.  $\ln [\text{OH}^-]$  was linear, its slope indicated that the rate was fractional order dependence on  $[\text{OH}^-]$  ( $n_{\text{ap}} = 0.16$ ).

### Rate dependence on $[\text{TeO}_4^{2-}]$

**TABLE 3: Effect of  $[\text{OH}^-]$  on rate**

[OH <sup>-</sup> ]/mol·dm <sup>-3</sup>	0.01	0.03	0.05	0.08	0.10
10 <sup>3</sup> $k_{\text{obs}}$ /s <sup>-1</sup>	11.55	14.16	15.30	16.26	16.85

[DTC] =  $2 \times 10^{-4}$  mol·dm<sup>-3</sup>,  $[\text{TeO}_4^{2-}] = 1 \times 10^{-3}$  mol·dm<sup>-3</sup>, [AA] =  $1 \times 10^{-2}$  mol·dm<sup>-3</sup>,  $\mu = 0.125$ , T = 25°C

At fixed [DTC], [AA],  $[\text{OH}^-]$ , ionic strength ( $m$ ) and temperature,  $k_{\text{obs}}$  decreased with the increase in  $[\text{TeO}_4^{2-}]$  (shown in TABLE 4). The plot of  $\ln k_{\text{obs}}$  vs.  $\ln [\text{TeO}_4^{2-}]$  was linear, its slope showed that the order with respect to  $[\text{TeO}_4^{2-}]$  was negative fractional ( $n_{\text{ap}}$

**TABLE 4: Effect of  $[\text{TeO}_4^{2-}]$  on rate**

$[\text{TeO}_4^{2-}]$ / mol·dm <sup>-3</sup>	0.001	0.003	0.006	0.008	0.010
10 <sup>3</sup> $k_{\text{obs}}$ /s <sup>-1</sup>	15.56	8.029	4.605	3.834	3.137

[DTC] =  $2 \times 10^{-4}$  mol·dm<sup>-3</sup>,  $[\text{OH}^-] = 0.1$  mol·dm<sup>-3</sup>, [AA] =  $1 \times 10^{-2}$  mol·dm<sup>-3</sup>,  $\mu = 0.125$ , T = 25°C

= -0.7).

### Effect of ionic strength on rate

At fixed [DTC], [AA],  $[\text{OH}^-]$ ,  $[\text{TeO}_4^{2-}]$  and temperature (25°C), rate constant  $k_{\text{obs}}$  decreases with the increase of  $\mu$  (shown in TABLE 5), which reveals that the effect of  $\mu$  on the rate is negative

**TABLE 5:  $k_{\text{obs}}$  in different ionic strength ( $\mu$ )**

$\mu$	0.1	0.15	0.2	0.25	0.3	0.35	0.4
10 <sup>3</sup> $k_{\text{obs}}$ /s <sup>-1</sup>	19.63	17.17	15.51	13.14	11.76	11.17	10.18

[DTC] =  $2 \times 10^{-4}$  mol·dm<sup>-3</sup>,  $[\text{OH}^-] = 0.1$  mol·dm<sup>-3</sup>, [AA] =  $2 \times 10^{-2}$  mol·dm<sup>-3</sup>,  $[\text{TeO}_4^{2-}] = 1 \times 10^{-3}$  mol·dm<sup>-3</sup>, T = 25°C

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