

Polarographic study of the kinetics of oxidation of allyl alcohol by chloramine-T

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Abstract. The kinetics of oxidation of allyl alcohol by chloramine-T (CAT) in presence of 0.02 M hydrochloric acid and at a constant ionic strength ($\mu=0.5$ M) have been studied polarographically at six different temperatures between 30°C and 45°C. The reaction shows first order dependence on concentration of chloramine-T. The energy and entropy of activation have been found to be 13.7 kcal mol⁻¹ and -28.4 e.u. respectively.

Keywords. Kinetics; allyl alcohol; chloramine-T; polarographic method.

1. Introduction

Chloramine-T (CAT) is one of the newer redox titrants and has been the subject of several recent studies (Berka *et al* 1965). Several organic compounds have been determined with this reagent, but very few kinetic investigations have been carried out with it. In most of the studies the progress of the reaction was followed by iodometric estimation of CAT in a measured aliquot of the reaction mixture at various time intervals. Mahadevappa and Naidu (1974) investigated the oxidation of allyl alcohol in 0.1M acid medium at 0-15°C with CAT by the iodometric method.

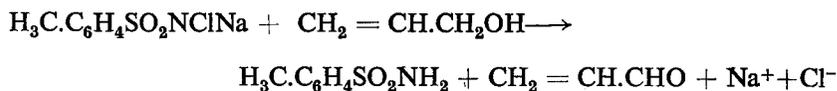
In the present investigation the kinetics of the oxidation of allyl alcohol in 0.02 M acid medium with CAT was studied by estimating the oxidant at suitable intervals by a convenient polarographic technique (Kolthoff and Lingane 1952).

2. Experimental

All solutions were prepared in double-distilled water. Allyl alcohol (E. Merck, b.p. 97.1°C) was purified and used. CAT was purified by the method of Morris *et al* (1948). Potassium chloride was used as the supporting electrolyte and also to provide a constant ionic strength. A manually operated polarograph (supplied by Paramount Electrical and Mechanical Industries, Poona) with a sensitive OSAW spot reflecting galvanometer was used. The polarographic cell with a dropping mercury electrode and an external saturated calomel electrode connected through an agar-KCl salt bridge was used in the measurements. The polarographic cell was kept immersed in a thermostat maintained at the required temperature. The com-

position of the solution studied was $[\text{CAT}] = 0.001\text{M}$; $[\text{Allyl alcohol}] = 0.05\text{M}$; $[\text{HCl}] = 0.02\text{M}$; $[\text{KCl}] = 0.5\text{M}$.

The reaction occurring between CAT and allyl alcohol may be represented by the following equation



The presence of allyl aldehyde (acrolein) in the reaction product was confirmed polarographically from its half-wave potential of -0.985 V vs SCE. Moshier (1943) reports a value of -1.04 V against mercury pool for acrolein.

The pH of the solution is not likely to change during the reaction. The pH was noted just at the start and after the reaction was over. Practically no change was observed.

3. Results and discussion

Preliminary experiments showed that $E_{1/2}$ of the oxidant was *ca* -0.08 V vs SCE. The limiting currents were measured for different concentrations of CAT employing a constant potential of -0.4 V versus SCE. The diffusion current due to the oxidant in the reaction mixture was evaluated from the difference in the galvanometer readings taken with and without the oxidant under identical conditions. A plot of concentration of CAT against the diffusion current was found to be linear (figure 1).

In the present investigation the progress of the reaction was followed by observing the galvanometer readings at suitable time intervals. The kinetics of the oxidation of allyl alcohol by CAT was studied at six different temperatures between $30\text{--}45^\circ\text{C}$. Plots of $\log(a-x)$ against time at each temperature were found to be linear (figure 2). The first order rate constants at different temperatures were then calculated from the corresponding slope. The data are given in table 1.

The rate constants obtained by Mahadevappa and Naidu (1974) are shown in table 2 for comparison.

Table 1. First order rate constants for the oxidation of allyl alcohol with CAT

Temp $^\circ\text{C}$	30	35	37.5	40	42.5	45
Rate constant $\times 10^3\text{ sec}^{-1}$	1.49	2.12	2.63	3.05	3.73	4.43

Table 2. Rate constants for the oxidation of allyl alcohol with CAT

$[\text{CAT}] = 0.005\text{M}$; $[\text{Allyl alcohol}] = 0.05\text{M}$; $[\text{H}^+] = 0.1\text{M}$; $\mu = 0.5\text{M}$

Temp $^\circ\text{C}$	0	5.5	8.1	10.9	15.8
Rate constant $\times 10^3\text{ sec}^{-1}$	0.120	0.200	0.263	0.335	0.513

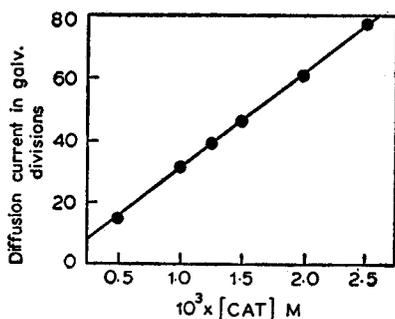


Figure 1. Plot of concentration of CAT against the diffusion current.

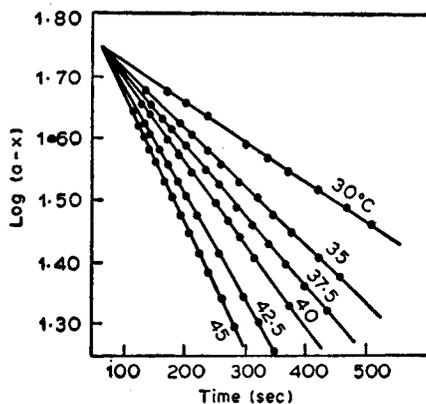


Figure 2. Plot of $\log(a-x)$ against time at six different temperatures.

The energy of activation was found to be $13.7 \text{ kcal mol}^{-1}$ from the slope of the linear plot of $\log k$ vs $1/T$. The entropy of activation was calculated and found to be -28.4 e.u. Mahadevappa and Naidu (1974) in a high acid concentration and low temperatures obtained the lower values viz. $12.3 \text{ kcal mol}^{-1}$ and -33.2 e.u. respectively.

4. Conclusion

Owing to the polarographic method of estimation of the oxidant, it has been possible to follow the reaction conveniently at much higher temperatures and with smaller concentrations of the reactants.

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