

Kinetics of Oxidation of Allyl Alcohol by Chloramine-T in Hydrochloric Acid Medium: Effect of High Acid Concentrations

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Abstract

The kinetics of oxidation of allyl alcohol by chloramine-T in presence of hydrochloric acid (0.15-0.29M) has been studied. At 0°C the rate is first order with respect to chloramine-T, second order in $[H^+]$ and independent of the alcohol concentration. The energy of activation and entropy of activation of the reaction have been found to be 55.6 kJ mol⁻¹ and -153 J K⁻¹ respectively. A mechanism is proposed.

The authors¹ have reported on the kinetics of reaction between allyl alcohol and chloramine-T in the presence of hydrochloric acid of concentration 0.04-0.13M at 0°C. The rate of disappearance of chloramine-T showed a first-order dependence on chloramine-T and $[H^+]$ and it was independent of the substrate concentration. In the present investigations we have examined the kinetic behaviour of oxidation with $[H^+]$ greater than 0.13M. However, at HCl concentrations beyond 0.29M, the rate becomes too rapid for kinetic measurements and with 0.2M HCl the reaction mixture becomes turbid due to the precipitation of dichloramine-T at chloramine-T concentrations greater than 0.008M. The kinetics was therefore studied at 0°C, within the above concentration limits of these reactants.

Experimental

The experimental procedures are described in the previous communication.¹ Allyl aldehyde was found to be the oxidation product of substrate^{1,2} even under these conditions.

Results

In the presence of excess alcohol and at constant $[H^+]$, the disappearance of chloramine-T obeys first-order kinetics and the pseudo-first-order rate constants calculated are given in Table 1. The rate is found to be independent of the substrate concentration. The concentration of HCl was varied from 0.15 to 0.29M and the rate is proportional to $[H^+]^2$ (Table 2). Further, a plot of $\log k_1$ against $\log[H^+]$ gave a straight line with slope 2. The reaction was carried out at different temperatures (0-11°C)

¹ Mahadevappa, D. S., and Naidu, H. M. K., *Aust. J. Chem.*, 1974, 27, 1203.

² Mahadevappa, D. S., and Naidu, H. M. K., *Talanta*, 1973, 20, 349.

and the energy of activation and entropy of activation were found to be 55.6 kJ mol^{-1} and -153 J K^{-1} respectively.

Table 1. Kinetics of oxidation of allyl alcohol by chloramine-T
At 0°C , μ 0.5M . Concentrations in mol l^{-1} , k_1 in min^{-1} , $[\text{H}^+]$ 0.2M

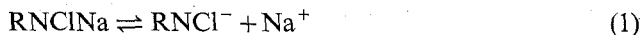
[chloramine-T] ₀	[alcohol] ₀	$10^2 k_1$	[chloramine-T] ₀	[alcohol] ₀	$10^2 k_1$
0.005	0.100	2.61	0.004	0.100	2.62
0.005	0.150	2.60	0.006	0.100	2.62
0.005	0.200	2.62	0.007	0.100	2.62
0.005	0.300	2.61	0.008	0.100	2.54
0.005	0.400	2.65			
0.005	0.500	2.67			

Table 2. Effect of $[\text{H}^+]$ on the reaction rate
[chloramine-T]₀ 0.005M ; [alcohol]₀ 0.1M ; μ 1.0M at 0°C

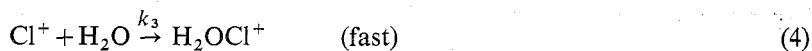
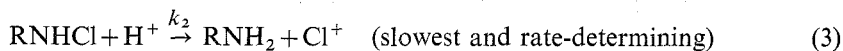
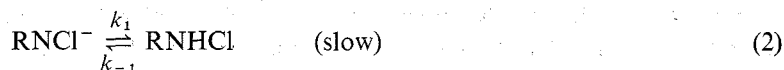
$[\text{H}^+]$	0.15	0.17	0.19	0.21	0.23	0.29
$10^2 k_1$	1.61	2.10	2.60	3.20	3.70	6.07
$10k_1/[\text{H}^+]^2$	7.16	7.27	7.20	7.26	7.19	7.22

Discussion

Chloramine-T being a strong electrolyte dissociates in aqueous solution as³



where $\text{R} = p\text{-MeC}_6\text{H}_4\text{SO}_2$. The active chlorine in the compound is assumed to be positive and, generally, chloramine-T undergoes a two-electron change per mole in all its oxidation reactions. Hence the following scheme is proposed for the release of Cl^+ ion, in a stepwise addition of two protons to the anion (equations (2) and (3)):



The chlorinium ion, not being a very reactive species,⁴ is rapidly converted into H_2OCl^+ (equation (4))^{5,6} which then attacks the substrate allyl alcohol in a fast step¹ to produce allyl aldehyde. Applying steady state conditions for RNHCl and taking $k_{-1} \gg k_2[\text{H}^+]$, the rate law

$$-d[\text{chloramine-T}]/dt = (k_1 k_2 / k_{-1}) [\text{chloramine-T}] [\text{H}^+]^2$$

can be derived in agreement with experimental results.

³ Bishop, E., and Jennings, V. J., *Talanta*, 1958, **1**, 197.

⁴ Swain, C. G., and Crist, D. R., *J. Amer. Chem. Soc.*, 1972, **94**, 3195.

⁵ De la Mare, P. B. D., Harvey, J. T., Hassan, M., and Varma, S., *J. Chem. Soc.*, 1958, 2756.

⁶ Wayman, M., and Thom, E. W. C. W., *Can. J. Chem.*, 1969, **47**, 2561.

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