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Kinetics and Mechanism of Oxidation of Cyclohexanol by 1-Chlorobenzotriazole (*CBT*) in Acid Medium

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The kinetics of oxidation of cyclohexanol by 1-Chlorobenzotriazole (*CBT*) has been studied at 40 °C in 50% aqueous acetic acid. The reaction is first order with respect to oxidant and first order with respect to substrate. The rate is found to increase with increase in acid concentration and percentage of *Ac*OH in the mixture. The kinetic parameters have been calculated. A suitable mechanism is proposed.

(Keywords: Cyclohexanol; Kinetics; Mechanism; Oxidation)

Kinetik und Mechanismus der Oxidation von Cyclohexanol mit 1-Chlorbenzotriazol (CBT) in saurem Medium

Die Kinetik der Oxidation von Cyclohexanol mit *CBT* wurde bei 40 °C in 50% wäßriger Essigsäure untersucht. Die Reaktion war sowohl bezüglich Oxidationsmittel als auch Substrat von erster Ordnung. Die Reaktionsgeschwindigkeit wird mit zunehmender Säurekonzentration (*Ac*OH) erhöht. Die kinetischen Parameter wurden bestimmt und ein passender Mechanismus wird vorgeschlagen.

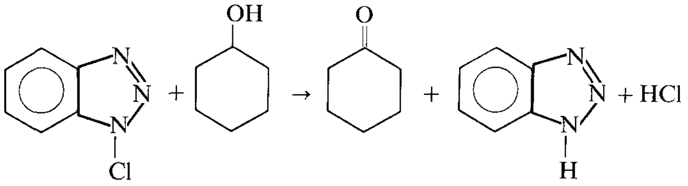
As a part of our programme to study the kinetics of oxidation of alcohols [1, 2], we now report in this paper the kinetics and mechanism of oxidation of cyclohexanol by *CBT* in acid medium. The kinetics of oxidation of cyclohexanol by a variety of metal cations [3–6], chloramine-T [7] and acid bromite [8] has been studied earlier.

Experimental

1-Chlorobenzotriazole was prepared [9] by the addition of a dilute solution of sodium hypochlorite to a 0.2 *M* solution of benzotriazole (E. Merck, melting point 96 °C) in 50% aqueous acetic acid (*v*/*v*). 1-Chlorobenzotriazole thus prepared was dried and recrystallised from methylene chloride-petroleum (m. p. 104–106 °C).

The purity of *CBT* was found to be 99% by iodometric assay. Analar grade acetic acid (BDH) was purified by the usual procedure. Cyclohexanol (BDH) was purified by distillation under reduced pressure. Analar perchloric acid, sodium perchlorate and sodium chloride were used as such. All kinetic measurements were carried out under pseudo-first order conditions and also in 50% *Ac*OH-50% H_2O (*v*/*v*). The kinetic measurements were made by estimating aliquot portions of the reaction mixture for the oxidant iodometrically using starch as indicator. The rate constants were evaluated from the plots of log $(a - x)$ vs. time, following the least squares method. The rate constants were reproducible within $\pm 3\%$.

Stoichiometry and Product Analysis: The reaction mixtures containing an excess of *CBT* over *CHOL* were kept at 40 °C under the kinetic conditions for 24 hours. Estimation of the unreacted *CBT* showed that 1 mol of *CHOL* consumed 1 mol of *CBT*. The product of oxidation (cyclohexanone) was confirmed by the isolation of its 2,4-dinitrophenylhydrazone [10].



CBT *CHOL* *CHON*

Results

The kinetics of oxidation of cyclohexanol by *CBT* was investigated at several initial concentrations of the reactants. The oxidation of cyclohexanol by *CBT* proceeds smoothly at 40 °C in aqueous acetic acid medium. At low concentrations of *CBT* and when cyclohexanol is in large excess, the reaction is found to be first order in *CBT*. The plots of log $(a - x)$ against time are found to be linear with a correlation coefficient > 0.99 (Table 1) showing a first order dependence on *CBT*.

The pseudo-first order constants in *CBT* (k_1) calculated at different initial concentrations of the substrate are found to increase linearly with the increase in cyclohexanol concentration. A plot of log k_1 against log [cyclohexanol] gave a straight line with slope unity, the correlation coefficient being 0.99 (Table 2).

The effect of hydrogen ion concentration on the rate of this oxidation is studied by varying $[H^+]$ while keeping the concentrations of other reactants constant. When $[HClO_4]$ was varied from 0.2 to 0.6 mol dm^{-3}, the first order rate constant varied from $2.56 \cdot 10^{-4}$ to $18.97 \cdot 10^{-4}\,s^{-1}$ (Table 2).

The increase in percentage of acetic acid in the reaction mixture increases the rate. A straight line is obtained when the percentage of acetic acid is plotted against the rate constant (Table 3).

Table 1. *Effect of [CBT] on the reaction rate at 40°*. [*CHOL*] = $1 \cdot 10^{-2}$ mol dm^{-3}; [*CBT*] = $1 \cdot 10^{-3}$ mol dm^{-3}; [$HClO_4$] = 0.400 mol dm^{-3}; [$NaClO_4$] = 0.400 mol dm^{-3}; solvent = 50% *Ac*OH, 50%H_2O (*v*/*v*)

Time s	[*CBT*]$_t \cdot 10^{-3}$ mol dm^{-3}	$k_1 \cdot 10^4$ s^{-1}
345	0.8515	4.66
820	0.6832	4.65
1 080	0.6040	4.67
1 390	0.5248	4.64
1 730	0.4455	4.67
2 100	0.3762	4.65
2 580	0.2970	4.70
3 080	0.2376	4.67

Correlation coefficient = 0.99

Table 2. *Effect of [Substrate] and* [H^+] *on the reaction rate at 40 °C.* [*CBT*] = $1 \cdot 10^{-3}$ mol dm^{-3}; [$NaClO_4$] = 0.400 mol dm^{-3}; solvent = 50% *Ac*OH, 50%H_2O (*v*/*v*)

[*CHOL*]$\cdot 10^2$ mol dm^{-3}	[$HClO_4$] mol dm^{-3}	$k_1 \cdot 10^4$ s^{-1}	$k_2 = \frac{k_1 \cdot 10^2}{[CHOL]}$ dm^3 mol^{-1} s^{-1}	
1.000	0.400	4.66	4.66	r = 0.99
2.000	0.400	9.37	4.68	
3.000	0.400	13.93	4.64	
4.000	0.400	18.13	4.53	
1.000	0.200	2.56		
1.000	0.300	4.03		
1.000	0.400	4.66		
1.000	0.500	7.04		
1.000	0.600	18.97		

Table 3. *Effect of solvent composition on the reaction rate at 40 °C.* [*CHOL*] = $1 \cdot 10^{-2}$ mol dm^{-3}; [*CBT*] = $1 \cdot 10^{-3}$ mol dm^{-3}; [$HClO_4$] = 0.400 mol dm^{-3}; [$NaClO_4$] = 0.400 mol dm^{-3}

[*Ac*OH—H_2O] % (*v*/*v*)	$k_1 \cdot 10^4$ s^{-1}
30–70	2.72
40–60	3.83
50–50	4.66
60–40	6.16
70–30	7.11

The reaction was carried out at different ionic strengths by altering the concentrations of $NaClO_4$ and keeping the concentrations of other reactants constant. Thus, when $[NaClO_4]$ was varied from 0.2 *M* to 0.8 *M*, the pseudofirst order rate constant varied from $2.69 \cdot 10^{-4}$ to $8.01 \cdot 10^{-4} s^{-1}$.

Even in the absence of chloride ions the rate of this oxidation is considerably fast. In presence of added Cl^- ions (0.01 *M*) the rate increases ten-fold.

The rate constants were measured at three different temperatures viz. 30°, 40° and 50 °C. The kinetic parameters are as follows:

$$E_a = 64.14\,\mathrm{kJ\,mol^{-1}};\ A = 5.32 \cdot 10^7\,\mathrm{s^{-1}};$$
$$\Delta S^{\ddagger} = -136.11\,\mathrm{JK^{-1}\,mol^{-1}};\ \Delta H^{\ddagger} = 61.63\,\mathrm{kJ\,mol^{-1}};$$
$$\Delta G^{\ddagger} = 102.88\,\mathrm{kJ\,mol^{-1}}\ (\text{at } 30\,^{\circ}\mathrm{C}).$$

Discussion

If $CBTH^+$ were the oxidising species one should expect an increase in the rate as $[HClO_4]$ increases; this is indeed what is observed in the present investigation. This kind of equilibrium between *CBT* and protonated *CBT* has been well established by previous studies [11, 12].

Increase in the dielectric constant of the medium shows a decrease in the rate constants. This observation is possible only if there is an ion-molecule involvement in the rate determining step. Furthermore, the increase in rate with the increase of ionic strength of the medium suggests the interaction of dipole-dipole; a rate law has been derived to explain satisfactorily the observed facts.

1. $CBT + H_3O^+ \overset{K}{\rightleftharpoons} CBTH^+ + H_2O$; fast

2. $CBTH^+ + CHOL \xrightarrow{k_1} CHON + BTH + 2\,H^+ + Cl^-$; slow

The rate equation becomes

$$-\frac{d\,[CBT]}{d\,t} = K \cdot k_1\,[CBT]\,[CHOL]\,[H^+]$$

Under constant $[H^+]$,

$$-\frac{d\,[CBT]}{d\,t} = k\,[CBT]\,[CHOL]$$

The above rate law explains the first order dependence of the reaction rate on the oxidant and the substrate.

An entirely different observation made by *Jeyaraman* et al. [13] in the reaction of cyclohexanone and *CBT* (viz. very low rate, absence of effect of ionic strength and zero order in *CBT* etc.) has ruled out the possibility of successive or competitive chlorination of substrate or product. Almost quantitative yield of cyclohexanone as the product also confirms this view.

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