LETTERS TO THE EDITOR

KINETICS AND MECHANISM OF THE OXIDATION OF DIMETHYL SULPHOXIDE BY SODIUM N-CHLORO BENZENESULPHONAMIDE IN HYDROCHLORIC ACID MEDIUM

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The kinetics of oxidation of substituted benzyl alcohols and cinnamyl alcohol by chloramine-B have been reported. Dimethyl sulphoxide (DMSO) is a versatile compound, widely used as a solvent, reaction medium and a chemical reactant. The present work reports the kinetics of oxidation of DMSO by CAB in HCl medium.

Experimental

Dimethyl sulphoxide (BDH) was distilled under reduced pressure and its aqueous solution was standardized by permanganometry. Chloramine-B (CAB) was prepared by the method described earlier. An aqueous solution of CAB was standardized by the iodometric method.

The kinetic studies were carried out at an ionic strength of 0.6 M (using NaClO3) at 0°C under pseudo first order conditions. The rate of reaction was determined by estimating the unreacted CAB iodometrically. The stoichiometry of the reaction was found to be 1:1 and the product was dimethyl sulphone as shown by TLC (Silica gel). The reaction can be represented as

\[ \text{C}_6\text{H}_5\text{SO}_2\text{NCa} + (\text{CH}_3)_2\text{SO} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{SO}_2\text{NH}_2 + (\text{CH}_3)_2\text{SO}_2 + \text{NaCl.} \]

Results and Discussion

At constant [H+] [0.2 M] and [DMSO] [0.1 M], a first order dependence of the rate on [CAB] (0.003-0.007 M) is noted. The pseudo first order rate constant \( k_p \) was \( 6.45 \times 10^{-4} \) sec\(^{-1}\). A plot of \( \log k_p \) vs. \( \log [\text{H}^+] \) gave a straight line of slope 0.66, indicating a fractional order dependence on substrate concentration (0.10-0.40 M). When HCl was varied from 0.15-0.40 M, a plot of \( \log k_p \) vs. \( \log [\text{HCl}] \) gave a straight line of slope 1.45. At constant [Cl\(^-\)] (kept at 0.40 M by adding NaCl), variation of [H\(^+\)] indicated a unit order dependence as shown by the constancy of \( k_p[\text{H}^+] \) values and also by a plot of \( \log k_p \) vs. \( \log [\text{H}^+] \). Keeping [H\(^+\)] constant at 0.2 M, [Cl\(^-\)] was varied by adding NaCl (0.20-0.50 M). A plot of \( \log k_p \) vs. \( \log [\text{Cl}^-] \) gave a straight line of slope 0.43.

Addition of the reaction product, benzene sulphonamide to the reaction mixture has no effect on the rate. Also, addition of methanol had a negligible effect on the rate indicating the absence of dielectric constant effects. Increase in the ionic strength of the medium from 0.6 to 1.2 M, increased the rate constant by about 22%, which is in the nature of a secondary salt effect, operating on equilibria encountered before the rate-determining step. Addition of acrylonitrile to the reaction mixture had no effect, indicating the absence of free radical species. The activation parameters were \( E_a = 65 \) kJ mole\(^{-1}\) and \( \Delta S^* = -82.5 \) JK\(^{-1}\).

In an acidified solution of CAB, the possible oxidizing species are dichloramine-B (RNCl), protonated CAB (RNHCl) and HOCI. If RNCl or HOCI were to be the active species, then the rate law will be contrary to experimental observations. It is likely that RNHCl oxidizes the substrate under the present conditions. The following scheme accounts for the experimental results:

\[ \begin{align*}
\text{RNCl}^- + \text{H}^+ & \rightleftharpoons \text{RNHCl} \quad \text{(i) fast equilibrium} \\
( K_t = k_1/k_2) \\
\text{RNHCl} + \text{DMSO} & \rightarrow X \quad \text{(ii) slow and rate determining} \\
( k_2) \\
X & \rightarrow \text{Products} \quad \text{(iii) fast} \\
\end{align*} \]

Assuming steady state conditions for RNHCl, rate law (1) is derived.

\[ \frac{d[CAB]}{dt} = \frac{k_1[DMSO][\text{H}^+]}{k_2 + k_3[DMSO]} \tag{1} \]

The mechanism of oxidation includes an electrophilic attack by the positive chlorine in RNHCl at the sulphur site of the substrate since the \( p\tau - d\tau \) overlap of the S-O bond leads to a considerable electron density. The reaction intermediate hydrolyzes through a fast step.

\[ \begin{align*}
\text{Me} & \quad \text{II} & \quad \text{Me} \\
\text{O} & \rightarrow \text{Me} & \rightarrow \text{Me} \\
(\text{i}) \quad \text{O} = \text{S} + \text{Cl} - \text{N} - \text{R} & \rightarrow \text{O} = \text{S} - \text{Cl} + \text{RNH}^- \\
\end{align*} \]
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SYNTHESIS WITH DIAZOALKANES AND $\alpha$-BENZOYL BENZOYL CHLORIDE

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$\alpha$-Benzoyl benzoyl chloride contains two sites of reactivity, the carbonyl group and an acid chloride group, both of which are susceptible towards diazoalkanes. By using different amounts of diazoalkanes it is possible to attack either one or both the sites present. The action of 2 moles of diazoalkanes on one mole of the acid chloride attacked only the acid chloride group while the carbonyl group, the other site, was also affected when 3 moles of diazoalkanes were used, resulting the $\alpha$-diazoketones.

$\alpha$-diazo-$\omega$-alkyl-$\omega$-benzoyl acetophenone (I) and $\alpha$-diazo-$\omega$-alkyl-$\omega$-1-alkyl-2-phenyl-1,2-epoxy-ethyl acetophenone(II) were synthesised by the action of 2 and 3 moles of diazoalkanes on $\alpha$-benzoyl benzoyl chloride (1 mol).

By adopting the method of Arndt, Eistert and Paralle$^{5}$ the action of 2 moles of diazomethane, diazoethane, diazo-1-propane, diazo-n-butane and phenyl diazomethane on $\alpha$-benzoyl benzoyl chloride in ether at 0°C was studied and diazoketons I (R = -H, -CH$_3$, -C$_2$H$_5$, -n-C$_3$H$_7$, and -C$_6$H$_5$) was obtained. When 3 moles of diazoalkanes were used the carbonyl group$^5$ was also attacked, resulting in the formation of II (R = -H, -CH$_3$, -C$_2$H$_5$, -n-C$_3$H$_7$, and -C$_6$H$_5$).

All these diazoketones were found to be orange or brown liquids, which could not be purified by distilla-