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KINETICS OF OXIDATION OF 2,6-DIPHENYLTETRAHYDROTHIOPYRAN-4- ONES BY PYRIDINIUM CHLOROCHROMATE

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Oxidation of cis- and trans-isomers of 2,6-diphenyltetrahydrothiopyran-4-one by pyridinium chlorochromate are found to be first order in each with respect to [subs] and [oxd]. Rate has been found to increase with increase in acid concentration and the rate dependence on $[H^+]$ is not unity. Based on the kinetic results suitable mechanism has been proposed.

INTRODUCTION

Oxidation of many compounds such as alcohols[1-3], aldehydes[4], sulphides[5] and ethers by pyridinium chlorochromate (PCC) have been investigated. The present work has been carried out to know the susceptibility of oxidising centres, namely, the ring sulphur and the carbonyl group in a heterocyclic system to the oxidant PCC. An attempt has also been made to know the effect of orientation of the phenyl groups present at C-2 and C-6 carbons on the rate of oxidation.

EXPERIMENTAL

The substrate and oxidant were prepared by known procedures. All the chemicals used were analytically pure.

RESULTS AND DISCUSSION

Kinetics of the oxidation of *cis*- and *trans*-2,6- diphenyltetrahydrothiopyrane-4-ones was studied under pseudo-first order condition in the presence of perchloric acid in aqueous acetic acid medium. Corresponding sulphoxides were found to be the product. The ionic strength of the medium was maintained constant by adding sodium perchlorate solution. The decrease in concentration of PCC was followed by iodometric method. Values of log $[PCC]_t$ *vs.* time in minutes were plotted and the pseudo-first order rate constants were evaluated from the slope of the straight line (Table 1). Results can be summarized as follows: The first-order rate constant for the oxidation reaction has been found to increase with increase in [subs]. A plot of k_0 against substrate concentration was linear, passing through origin showing first order dependence of rate on [subs]. Plot for different concentrations of PCC was linear and the rate constants was independent of the initial concentration of PCC, showing first order dependence of rate on PCC also. Rate constant of the reaction increased significantly with increase in $[H^+]$. As the plot of log k_0 against $[H^+]$ was linear and did not pass through the origin, the rate of the reaction was not unity with respect to [H^+]. The rate constants observed for different perchlorate concentrations showed the independent nature of the reaction on the ionic strength of the medium. Effect of dielectric constant of the medium on the rate of the reaction was studied by varying the percentage of acetic acid from 50–70%. It has been found that the rate constant increased with decrease in dielectric constant of the medium. The kinetics of the reaction was studied at various temperatures to find out the effect of temperature on the reaction rate and to compute the activation parameters. Rate of the reaction increased with increase in temperature and from the slope of the Arrhenius plot, the activation parameters were calculated and presented in Table 1. Oxidation of *trans* isomer was carried out at different temperatures under similar conditions as that of *cis* isomer in order to compare the rate constants for both and found that *trans* isomer reacted at a faster rate compared to *cis* isomer.

TABLE 1
KINETIC AND ACTIVATION PARAMETERS

Substrate	k_2 $M^{-1}\ m^{-1}$ at 30°C	E_a (KJ mol^{-1})	$H^{\ddagger}$ (KJ mol^{-1})	$S^{\ddagger}$ (J $deg^{-1}\ mol^{-1}$)
cis-Isomer	3.84	42.13	39.62	–127.68
trans-Isomer	8.81	38.30	35.78	–142.99

With the aid of literature evidence[5] and the present observations, a suitable mechanism has been proposed for the oxidation of *cis*- and *trans*-2,6-diphenyltetrahydrothiopyran-4-ones by PCC.

$$PCC + H^+ \rightleftharpoons PCCH^+ \qquad \text{(i)}$$

$$\rangle S + PCCH^+ \xrightarrow{\text{slow}} \rangle S{-}PCCH^+ \qquad \text{(ii)}$$

$$\rangle S - PCCH^+ \xrightarrow{\text{fast}} \rangle S{=}O + \text{other products} \qquad \text{(iii)}$$

PCC gets protonated in the first step and is found to be an effective species in acidic medium. This protonated PCC interacts with sulphide in a slow step to form an intermediate complex which decomposes in a final step to form sulphoxide and other products. The increase in rate constants with increase in acid concentration and acetic acid percentage of the medium favours the involvement of protonated PCC in rate determining step. The negative entropy of activation indicates the formation of the complex intermediate in a slow step. This has been further supported by the oxidation of aryl alkyl sulphides by PCC[5] and bromine[9] where same type of mechanism has been predicted. Another interesting factor is that the *trans* isomer reacted at a faster rate than the *cis* as the complex formation is the rate-determining step. If complex decomposition into products takes place by a slow step, the reverse trend would be observed due to the difference in the orientation of adjacent phenyl groups in both isomers.

The difference in rate constants between *cis*- and *trans*-2,6-diphenyltetrahydrothiopyran-4-ones (Table 1) can be explained on the basis of effect of orientation of phenyl groups. The faster rate of oxidation of *trans* isomer shows that intermediate complex formation is easier in this case compared to *cis* isomer. This is because the orientation of phenyl groups in *trans* compound is such that the approach of PCC to the ring sulphur is less hindered. The approach of protonated PCC to the ring sulphide to form the intermediate complex is difficult in *cis* isomer due to non-bonded interactions of the diequatorially oriented phenyl groups. An examination of Drieding models also reveals that the approach may be difficult in *cis* isomer. In the *trans* isomer where one of the phenyl groups is axially oriented, steric effect is less significant. The results obtained in this present investigation lead to the conclusion that a reaction in which a complex formation (rate determining set) is envisaged involving the sulphur atom at 1-position with the two phenyl groups with equatorial orientation on adjacent carbons retards the complex formation. When one of the 2,6-phenyl groups is axially oriented the approach of the reagent to 1-position is less hindered.

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