

Kinetics and mechanism of oxidation of chalcones by trichloroisocyanuric acid [TCICA] in HOAc-HClO₄ medium

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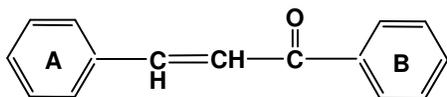
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The kinetics and mechanism of oxidation of chalcone and some substituted chalcones by trichloroisocyanuric acid (TCICA) has been investigated at 313 K in HOAc-HClO₄ medium. The reaction has been found to be first order each in [TCICA] and [Chalcone] and fractional order in [H⁺]. There is no kinetic or spectral evidence for the formation of complex between TCICA and Chalcone. The rate increases with increase in percentage of acetic acid and [Cl⁻]. The products of oxidation have been identified as phenyl acetaldehyde and benzoic acid. The reactive species of oxidant have been established as HOCl and H₂OCl⁺. The rate increases with electron releasing groups in the benzaldehyde moiety and vice versa with a Hammett's ρ value of -0.45. A suitable mechanism involving the chalcone molecule and the reactive species of TCICA in the rate determining step has also been proposed.

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In recent years, the kinetic studies on the oxidation as well as halogenation of organic compounds by N-halo compounds is gaining importance due to their applications in organic synthesis and also due to the kinetic aspects¹⁻⁵. In all these N-halo compounds, N-X bond is highly polar, and they produce positive halogen (X⁺) in polar solvents due to protonation or hydrolysis. This positive halogen acts as powerful electrophile. Among the N-halo compounds, trichloroisocyanuric acid (TCICA), or 1,3,5-trichloro-1(H),3(H),5(H)-triazine-2,4,6-trione has wide synthetic utility as it has more polar N-X bond. Literature survey reveals that there are no kinetic and mechanistic studies involving this useful compound with chalcones. Chalcones or phenyl styryl ketones are of interest because they have a unique structural feature of having a >C=O functional group in conjugation with >C=C< and the whole molecule is in conjugation



Chalcones are oxidized by different oxidizing agents and in all these reactions either the >C=C< or >C=O group of the chalcone is attacked by the oxidant⁶⁻¹¹. The trace metal ion catalysis of Os(VIII)¹² and Ru(III)¹³ with various one and two equivalent oxidants was also studied in the oxidation of chalcones. The present investigation of TCICA oxidation of chalcone and some substituted chalcones was undertaken in HClO₄-HOAc medium to ascertain: (i) the site of attack of the oxidant, and (ii) the effect of substituents on the rate of reaction.

Experimental

The TCICA solution was prepared in acetic acid and standardized by the iodometric method and preserved in amber coloured bottles. Chalcones were prepared by standard methods¹⁴. The solution of chalcones was prepared in pure acetic acid. Acetic acid was purified by the method of Orton and Bradfield¹⁵. All other chemicals were of accepted grades of purity. Under pseudo first order conditions there are solubility problems of chalcone in acetic acid-water mixtures and also the rate is very fast under these conditions. Hence, the kinetics of these reactions was studied under second order conditions. The rates were followed by estimating the unreacted [oxidant] iodometrically at regular intervals of time. The initial rates were evaluated from the plots of [oxidant] versus time plots and were reproducible within ±2%. The reaction products, phenyl acetaldehyde and benzoic acid were detected by TLC and compared with those of the authentic samples. The presence of aldehyde among the reaction products was also detected by preparing their 2,4-dinitrophenyl hydrazone derivatives.

Results and discussion

The orders were determined using initial rate method. The order with respect to [TCICA] was found to be unity as revealed by the slope of the linear plot of the log[initial rate] versus log[TCICA]. The order in [chalcone] was also found to be unity as obtained from the slope of the linear plot of log [initial rate] versus log [chalcone]. This was found to be true for all the chalcones studied. The Michaelis-Menten type of reciprocal plot of 1/[IR] [IR = initial rate] versus 1/[chalcone] was linear passing through

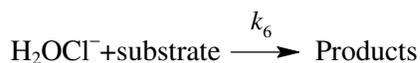
the origin indicating the absence of complex formation or lack of kinetically detectable complex between chalcone and TCICA. Addition of monomers like acrylonitrile to the reaction mixture under inert conditions did not induce any polymerization indicating the absence of free radicals in the reaction mixture. The rate increased with an increase in $[\text{HClO}_4]$. For instance, under the conditions of $[\text{TCICA}] = 3.0 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{chalcone}] = 3.0 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{HOAc}] = 80.0\% \text{ (v/v)}$; $\text{temp} = 313 \text{ K}$, the initial rate ($\text{IR} \times 10^7 \text{ mol.dm}^{-3} \cdot \text{s}^{-1}$) increased from 3.47 to 6.94 for an increase of $[\text{HClO}_4]$ from 0.025 to 0.100 mol.dm^{-3} respectively. The log-log plot of initial rate against $[\text{HClO}_4]$ gave a straight line with a slope of 0.51 indicating that order with respect to $[\text{H}^+]$ is fractional. Such fractional orders with respect to $[\text{H}^+]$ are also observed in several electron transfer reactions¹⁶. Increase in the percentage composition of acetic acid in the reaction mixture increased the rate and a linear plot with positive slope was obtained by plotting $\log [\text{IR}]$ versus $1/D$ (where D is the dielectric constant of the medium). The positive slope indicates the reaction to be of positive ion-dipole type. The rate is not affected by the addition of isocyanuric acid to the reaction mixture. The rate increased by increasing the $[\text{Cl}^-]$. For example under the conditions of $[\text{TCICA}] = 3.0 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{chalcone}] = 3.0 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{HOCl}] = 0.05 \text{ mol.dm}^{-3}$; $[\text{HOAc}] = 80.0\% \text{ (v/v)}$; $\text{temp} = 313 \text{ K}$, the initial rate increased from $5.27 \times 10^{-7} \text{ mol.dm}^{-3} \cdot \text{s}^{-1}$ to $8.47 \times 10^{-7} \text{ mol.dm}^{-3} \cdot \text{s}^{-1}$ by increasing the $[\text{Cl}^-]$ ions from $0.500 \times 10^{-3} \text{ mol.dm}^{-3}$ to $2.50 \times 10^{-3} \text{ mol.dm}^{-3}$. This increase in rate may be attributed to the formation of molecular chlorine as per the equation: $\text{H}_2\text{OCl}^+ + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ (where H_2OCl^+ is the reactive species liberated by the hydrolysis of TCICA). The molecular chlorine, thus formed, will get involved in the oxidation process along with TCICA and increase the rate rapidly. The products of oxidation were identified as benzoic acid and phenyl acetaldehyde for simple chalcone. The unit orders with respect to $[\text{TCICA}]$ and $[\text{chalcone}]$ indicate that probably they are not involved in the formation of any kind of complex, or even if the complex is formed it was assumed to be highly unstable. The lack of stable complex was also supported by the double reciprocal plot of $1/[\text{IR}]$ versus $1/[\text{chalcone}]$ which passes through the origin. In strongly acidic media, TCICA may get protonated producing electrophilic species¹⁷ and these species will get hydrolysed in the presence of acid to give the reactive species such as HOCl and H_2OCl^+ . The hydrolysis constants of various species of TCICA are

reported in literature¹⁸. From these equilibrium constant values, it is clear that the concentrations of mono chloroisocyanuric acid (MCICA) and isocyanuric acid (ICA) would be negligible in acid medium as the values of $(K_1.K_2.K_3)$ and $(K_1.K_2)$ are negligible in comparison to K_1 . Hence, the first stage of hydrolysis seems to be kinetically important one. Therefore, the predominant reactive species is assumed to be HOCl. The increase in rate with increase in $[\text{H}^+]$ indicates that probably HOCl may enter into protonation equilibrium giving H_2OCl^+ . Thus, the reactive species may therefore, be assumed to be HOCl and H_2OCl^+ . The rate decreased considerably with the addition of $\text{Hg}(\text{OAc})_2$. This may be attributed to the removal of reactive species HOCl and H_2OCl^+ by acetate ions as CH_3COOCl .

Chalcone contains two functional groups, viz. $>\text{C}=\text{C}<$ and $>\text{C}=\text{O}$, and the whole molecule is in conjugation. It is possible for HOCl or H_2OCl^+ , the reactive species of TCICA, to attack either at $>\text{C}=\text{C}<$ or at $>\text{C}=\text{O}$ or as an alternative path these can chlorinate phenyl rings. As no chlorination products were detected, the nuclear chlorination of phenyl rings was ruled out. The other possibility is the attack at $>\text{C}=\text{C}<$ or $>\text{C}=\text{O}$. The functional group $>\text{C}=\text{C}<$ may not be attacked by HOCl as $>\text{C}=\text{C}<$ group is deactivated by two phenyl rings in conjugation. The other alternative is the attack at $>\text{C}=\text{O}$. The keto functional group is highly polarized and HOCl forms an unstable intermediate complex with chalcone at this site. This unstable complex decomposes in a rate determining step to give the final products, viz. benzoic acid and phenyl acetaldehyde.

Based on the above experimental observations the most probable mechanism is shown in Scheme 1.

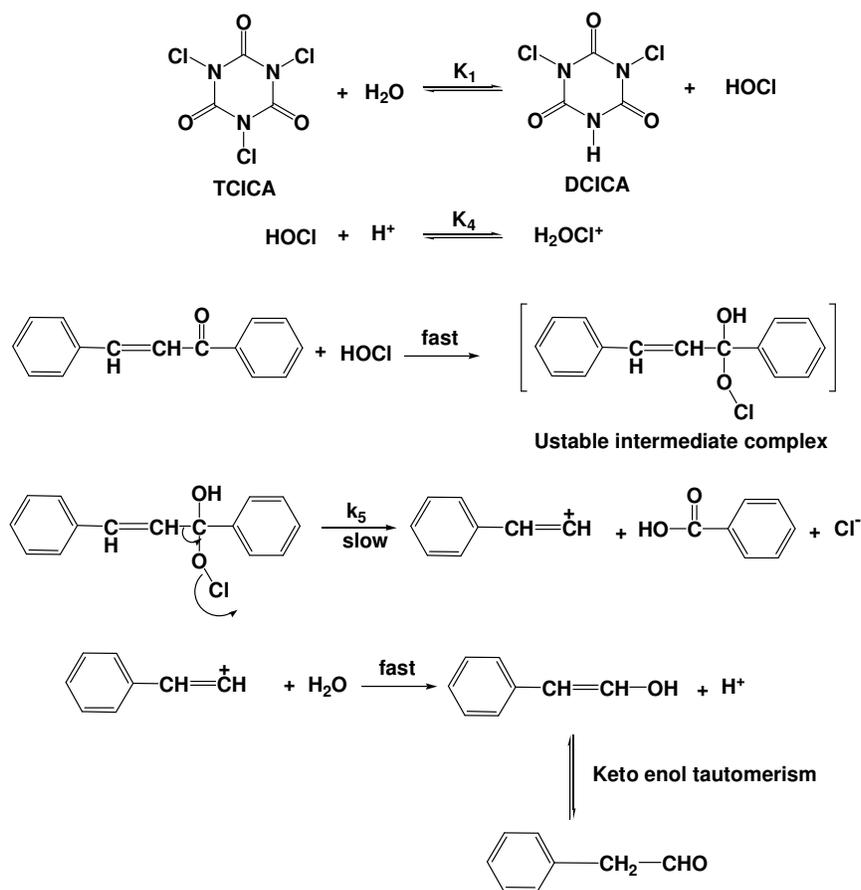
Similar mechanism can be written taking H_2OCl^+ as the reactive species:



From the above mechanism, the following rate law could be derived:

$$\begin{aligned} -\frac{d \ln[\text{TCICA}]}{dt} &= k_{\text{obs}} \\ &= \frac{K_1 k_5 [\text{chalcone}] + K_1 K_4 k_6 [\text{chalcone}] [\text{H}^+]}{K_1 + K_1 K_4 [\text{H}^+]} \end{aligned}$$

The above rate law explains the observed unit order dependence of rate each on $[\text{substrate}]$ and $[\text{TCICA}]$ and fractional order dependence on $[\text{H}^+]$.



Scheme 1

The structure-reactivity relationships

The effect of substituents in the benzaldehyde ring (ring A) on the rate was studied taking chalcone and six substituted chalcones. The rates were found to follow the order: $p\text{-OCH}_3 > p\text{-CH}_3 > \text{H} > p\text{-Cl} > m\text{-Cl} > m\text{-NO}_2 > p\text{-NO}_2$. It is clear from the data that electron releasing groups increase the rate and vice versa. The Hammett's plot of $\log k''$ versus σ gave a straight line with a slope of (ρ) = -0.45 ($r = 0.994$). The negative ρ value indicates that the reaction is favoured by high electron density at the reaction centre in the transition state. The correlation of both para and meta substituents with the single σ value indicates that the polar effects of the substituents are more important than the resonance effects. The small ρ value (-0.45) indicates that the charge development in the transition state is small in this reaction as the whole molecule is in conjugation.

Effect of temperature and isokinetic phenomenon

The rates of oxidation were determined at different temperatures and the Arrhenius plots of $\log k''$ versus

Table 1 — Activation parameters for the oxidation of chalcones by TCICA in $\text{HClO}_4\text{-HOAc}$ medium ($[\text{TCICA}] = 3.00 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{substrate}] = 3.00 \times 10^{-3} \text{ mol.dm}^{-3}$; $[\text{HClO}_4] = 0.05 \text{ mol.dm}^{-3}$; $[\text{HOAc}] = 80.0\% \text{ (v/v)}$; Temp. = 313 K)

Substituent	$k'' \times 10^2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	$-\Delta S^*$ ($\text{J deg}^{-1} \text{mol}^{-1}$)
$p\text{-NO}_2$	2.69	45.2	86.2	131
$m\text{-NO}_2$	2.88	40.3	86.0	146
$m\text{-Cl}$	4.17	39.5	85.1	146
$p\text{-Cl}$	4.78	33.8	84.7	163
H	5.56	29.9	84.3	174
$p\text{-CH}_3$	6.94	26.1	83.7	184
$p\text{-OCH}_3$	8.02	23.2	83.4	192

$1/T$ were all linear. From these plots, the activation parameters like ΔH^* , ΔG^* , ΔS^* were calculated and the same are given in Table 1. It is clear from these values that both the parameters ΔH^* and ΔS^* are important in controlling the rates of reactions though the enthalpy factor appears to be more predominating. The ΔS^* values are negative indicating the loss of

entropy during the formation of activated complex. The isokinetic temperature (β) was calculated from the slope of linear plot of ΔH^* versus ΔS^* and found to be 361 K. The ' β ' value is above the experimental temperature range (298 – 313 K) used in the present study indicating that the reactions are enthalpy controlled. Using the appropriate statistical techniques, Exner¹⁹ showed that ΔH^* versus ΔS^* relationship exists only when $\log k_2''$ versus $\log k_1''$ is linear (k_1'' and k_2'' are rate constants at temperature T_1 and T_2 , where $T_2 > T_1$). The Exner plot of $\log k_2''$ at 313 K against $\log k_1''$ at 303 K was linear with a slope of 0.65. From this value of slope, the isokinetic temperature was calculated and found to be 347 K which is in agreement with the value obtained from the plot of ΔH^* versus ΔS^* . The isokinetic correlation implies that all the chalcones are oxidized by the same mechanism and the changes in rate of oxidation is governed by the changes in both the ΔH^* and ΔS^* values. The constancy of ΔG^* values for all the chalcones studied indicate that probably the same mechanism is operative in all these cases.

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