



Kinetics of Oxidation of 3-Benzoylpropionic Acid by *N*-Chlorobenzamide in Aqueous Acetic Acid Medium

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Abstract: The kinetics of oxidation of 3-benzoylpropionic acid (KA) by *N*-chlorobenzamide (NCB) in aqueous acetic acid medium in the presence of perchloric acid have been investigated. The observed rate of oxidation is first order dependence each in [KA], [NCB] and [H⁺]. The main product of the oxidation is the corresponding carboxylic acid. The rate decreases with the addition of benzamide, one of the products of the reaction. Variation in ionic strength of the reaction medium has no significant effect on the rate of oxidation. But the rate of the reaction is enhanced by lowering the dielectric constant of the reaction medium. Hypochlorous acidium ion (H₂O⁺Cl), has been postulated as the reactive oxidizing species. A mechanism consistent with observed results have been proposed and the related rate law deduced. The activation parameters have been computed with respect to slow step of the mechanism.

Keywords: Kinetics, Oxidation, *N*-Chlorobenzamide, 4-Oxoacids, 3-Benzoylpropionic acid.

Introduction

The chemistry of reactions of *N*-halo compounds form a separate branch, which is a great synthetic importance¹. *N*-Halo compounds have been extensively employed as oxidizing agents for organic substrates²⁻³. In the recent development, *N*-halo compounds are the source of positive halogen and have been exploited as oxidant for a variety of substrates in both acidic and alkaline media. The nature of active oxidizing species and mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction conditions. Although a lot of works have been reported on the oxidation of organic compounds by *N*-halo compounds⁴⁻⁷, it is to be noted that no systematic kinetic investigation on the oxidation of 3-benzoylpropionic acid by *N*-chlorobenzamide has yet been reported in the literature. Here we report the results of the kinetics of the oxidation of 3-benzoylpropionic acid (KA) with *N*-chlorobenzamide (NCB) in aqueous acetic acid medium in the presence of perchloric acid.

Experimental

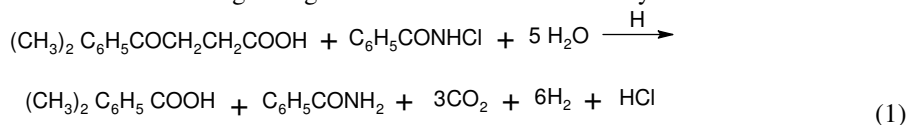
The solutions of 3-benzoylpropionic acid and *N*-chlorobenzamide were prepared using doubly distilled water. Standard solution of NCB was prepared afresh. Perchloric acid (AnalaR) was used as source of hydrogen ions. Sodium perchlorate (Merck) was used to keep the ionic strength constant.

The reaction was carried out under pseudo-first order condition ($[KA] \gg [NCB]$). The reaction was followed by potentiometrically by setting up a cell made up of the reaction mixture into which the platinum electrode and reference electrode (SCE) were dipped. The emf of the cell was measured periodically using a Equip-Tronic potentiometer, while the reaction mixture was continuously stirred. The pseudo-first order rate constants computed from the plots of $\log (E_t - E_\infty)$ against time were reproducible within $\pm 3\%$.

Results and Discussion

Stoichiometry and reaction products

Different sets of reaction mixtures containing different quantities of NCB and KA at constant $[H^+]$ and ionic strength were reacted for 24 h at $30^\circ C$ and then analyzed. The remaining NCB was estimated. The oxidation products were identified as benzoic acid and benzamide. It was confirmed by noting the mixed melting point, chemical methods and TLC techniques. The results are in good agreement with 1:1 stoichiometry.



Reaction order

The reaction orders were determined from the slopes of $\log k_1$ versus \log (concentration) plots by varying the concentration of substrate (KA) and perchloric acid in turn while keeping others constant. The plot $\log k_1$ against $\log [KA]$ is linear ($r = 0.995$) with a slope value of 1.003 and the plot $\log k_1$ against $\log [H^+]$ is also linear ($r = 0.998$) with a unit slope. This is further supported by the fact that the plots of k_1 versus $[KA]$ and k_1 versus $[H^+]$ gives a straight line passing through the origin, the linearity of the plots of $\log [NCB]$ versus time indicates the order in $[NCB]$ as unity, this is also confirmed by constant values of k_1 at varying $[NCB]$ (Table 1). This indicates clearly that the reaction is first order with respect to $[KA]$, $[NCB]$ and $[H^+]$.

Table 1. Rate constant for the oxidation of 3-benzoylpropionic acid by NCB in aqueous acetic acid medium at $30^\circ C^a$

$10^2 [KA]$ mol dm ⁻³	$10^3 [NCB]$ mol dm ⁻³	$[H^+]$ mol dm ⁻³	$10^4 k_1^b, s^{-1}$	$10^3 k_2^c$ dm ³ mol ⁻¹ s ⁻¹
2.0	1.0	0.5	2.123	10.62
3.0	1.0	0.5	3.121	10.40
4.0	1.0	0.5	4.211	10.53
5.0	1.0	0.5	5.352	10.70
6.0	1.0	0.5	6.288	10.48
2.0	1.0	0.8	3.442	0.43
2.0	1.0	1.2	5.016	0.42
2.0	1.0	1.4	6.011	0.43
2.0	1.2	0.5	2.23	-
2.0	1.4	0.5	2.35	-
2.0	1.8	0.5	2.14	-
2.0	2.0	0.5	2.26	-

^a General conditions: $[NaClO_4] = 0.5$ mol dm⁻³, Solvent composition: 50% Acetic acid – 50% Water (v/v). ^b Estimated from pseudo-first order plots, the error quoted in k_1 values is the 95% confidential limit of 'Student *t*' test. ^c Individual k_2 values estimated as $k_1 / [KA]$ or $k_1 / [H^+]$

Effect of products

The effect of product, benzamide was studied in the concentration range 0.04 - 0.1 mol dm⁻³. The addition of benzamide reduced the rate of oxidation of keto acid.

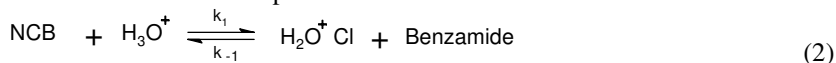
The effect of dielectric constant in the reaction medium was studied by adding acetic acid (50%-80%) in the reaction medium at constant concentrations of other reactants. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. The effect of ionic strength was studied by varying the concentration of NaClO₄ in the reaction medium. It was found that the rate of reaction is independent of ionic strength of the medium. The reaction mixture was kept for 24 h with acrylonitrile in an inert atmosphere. Test for free radical was negative.

The effect of temperature

The rate of reaction was measured at different temperatures. The activation parameters for the oxidation of keto acid by NCB have been evaluated from the slope of the Arrhenius plots.

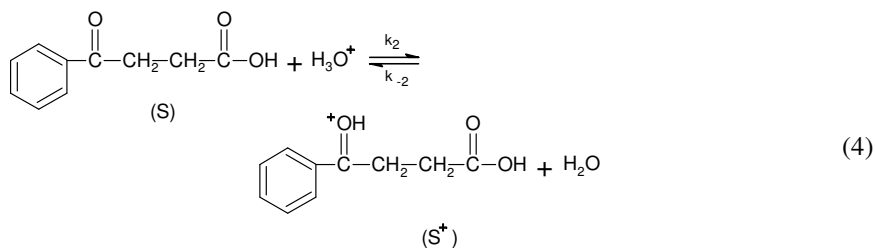
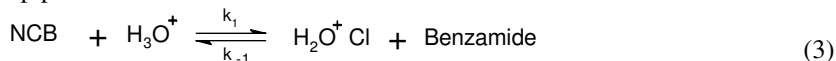
Mechanism

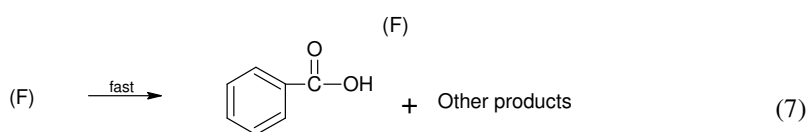
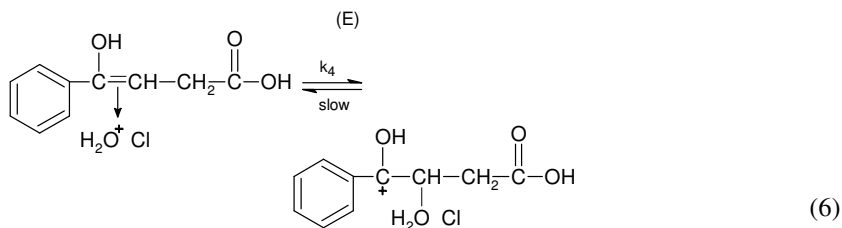
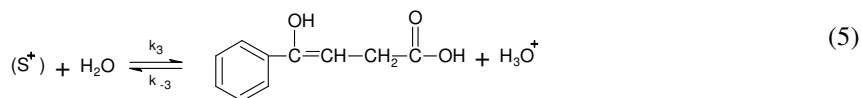
It is known that⁹ the probable reactive species of NCB in acid solution, H₂O⁺Cl. The reaction is first order in [NCB], [KA] and [H⁺]. The reaction rate increases with increase in [H⁺] at constant ionic strength, showing that the reaction proceeds completely through the acid-catalyzed pathway. The change in the polarity of the medium has a marked effect on the reaction rate. The trend in the rate observed may be due to more than one factor. It may be attributed to the lowering of dielectric constant of the medium which favors reaction involving protonation. Further, the enolization of the keto acid may be catalyzed by acetic acid and this may also contribute to rate enhancement. The plot of log k₁ versus 1/D is linear (r = 0.991) with positive slope, indicating an interaction between a positive ion and a dipole molecule. This supports the postulation of (H₂O⁺Cl) as the reactive species. The retardation of reaction rate on the addition of saccharin suggests¹⁰ a pre-equilibrium step involves a process in which saccharin is one of the products.



If this equilibrium is involved in the oxidation process, the retardation should be an inverse function of saccharin concentration, which is borne out by observation that the inverse of the rate constant gives a linear (r = 0.992) plot against [Benzamide].

A mechanism has been proposed involving the attack of H₂O⁺Cl on the enol form of the substrate (E) in the rate determining step. It is known⁹ that the enolization is proposed to be the necessary step prior to the oxidation of the substrate



**Scheme 1**

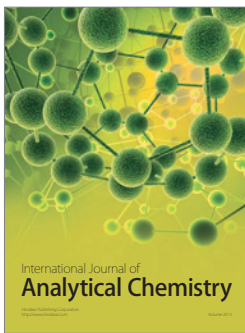
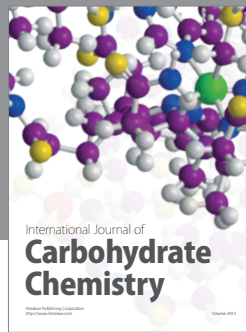
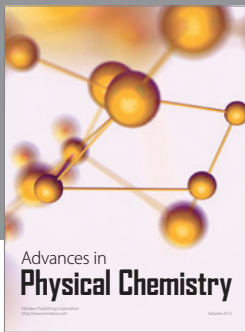
Scheme 1 leads to rate law (8)

$$\frac{-d[\text{NCB}]}{dt} = \frac{k_2 k_3 k_4 [\text{S}][\text{H}_3\text{O}^+][\text{H}_2\text{O}^+\text{Cl}]}{k_{-2} k_{-3} k_a [\text{Benz}]} \quad (8)$$

Eq (8) clearly points out the observed results *i.e.* first order in [KA], [NCB], [H⁺] and inverse order in [Benzamide] on the rate of the oxidation.

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