

SUBSTITUENT EFFECTS: KINETICS AND MECHANISM OF OXIDATION OF SOME ARYL THIOACETIC ACIDS BY DICHLOROISOCYANURIC ACID (DCICA)

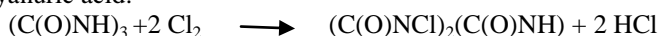
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ABSTRACT

The kinetics of oxidation of meta- and para-substituted phenylthioacetic acids with Dichloroisocyanuric acid in aqueous acid (80% v/v) has been measured at 30°, 40° and 50°C. The reaction follows an overall second order kinetics, first order each in phenylthioacetic acid and Dichloroisocyanuric acid. In the present investigation, it is considered to study the kinetics of oxidation of some arylthioacetic acids and some mono substituted phenylthioacetic acids by Dichloroisocyanuric acid (DCICA). Dichloroisocyanuric acid colourless solid is the active ingredient in commercial bactericides, algicides and cleaning agents. It is an oxidizer that reacts with water to form hypochlorous acid, a compound related to the active ingredient in bleach. It is manufactured by chlorination of cyanuric acid:

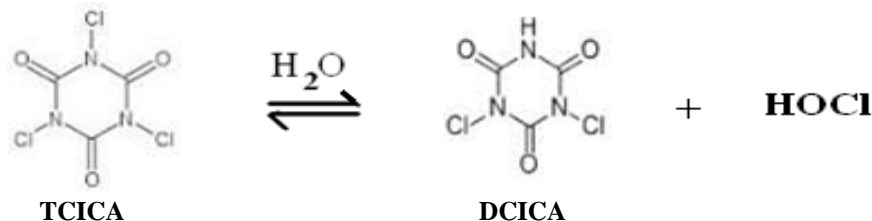


Several studies have been made on the kinetics of oxidation of organo sulphur compounds. Mechanism and rate of oxidation of these compounds was found to be largely dependent on the nature of the oxidizing agents. Extensive studies on the mechanism of oxidation of sulphides to sulfoxides by several oxidants were reported. However, a survey of literature revealed that only a few metal ions like Mn(III), V(V), Fe(III) and Mn(V) are used for the oxidation of sulfides and sulfoxides. No attempt was made for the oxidation of aryl thio acetic acids by Dichloro Isocyanuric acid (DCICA).

A possible mechanism for the oxidation of PTAA with DCICA is suggested. The influences of temperature, solvent medium and composition on the rate of oxidation of DCICA are studied.

Scheme:

Trichloro isocyanuric acid is hydrolyzed in aqueous solutions forming Dichloro Isocyanuric acid and Monochloro Isocyanuric acid.



KEY WORDS: Oxidation, arylthioacetic acids, Kinetics, Mechanism.

INTRODUCTION

An important step towards a quantitative explanation of the effect of substituent's reactivity is to find empirical correlations, whereby one body of the results can be related to another, and quantitative estimates of the factors underlying reactivity can be obtained. Of course the problem of transmission of substituent effects across a molecule is highly complex. Jaffé calculated the effect of substituent's on the reaction centre in various aromatic systems on the assumption that the substituent's act only by polarizing the π -electrons. However, it was found that the dissociation constants of substituted bicyclo [2.2.2] octane-1-carboxylic acids (I) and substituted cubanecarboxylic acids (II) are comparable in nature to that of the dissociation constants of substituted benzoic acids.

This clearly indicates that the lack of π -electrons does not in any way affect the transmission of the substituent effects. A substituent can influence the reaction centre at least in five different ways: (a) The electric dipole field of the polar substituent-substrate bond can influence the reaction centre across space (field effect), (b) the primary inductive effect can be transmitted to the reaction centre by successive polarization of the intervening σ -bonds (σ -inductive effect), (c) the electrostatic charge set up at a conjugate atom, adjacent to the substituent may polarize the corresponding π -electron system, (d) the π -electron system can also be polarized by resonance interaction with the substituent (mesomeric effect), (e) the electromeric effect which has importance when there is mutual conjugation between the substituent and the reaction centre. The importance of these various effects is of course familiar from many examples. The well-known Hammett equation is

$$\log \frac{k}{k_0} = \rho \sigma$$

Where, k and k_0 are the rate or equilibrium constants for reactions of the substituted and unsubstituted compounds, respectively; σ is the substituent constant which depends on the nature and position of the substituent, ρ is the reaction constant which depends on the nature of the reaction, solvent and temperature.

Table.1.Hammett substituent constants

Substituent	Substituent constants σ -values	
	Meta	Para
F	+0.337	+0.062
Cl	+0.373	+0.227
Br	+0.391	+0.232
I	+0.350	+0.180
CH ₃	-0.069	-0.170
OCH ₃	+0.115	-0.268
NO ₂	+0.710	+0.778

In Table 2 are given σ^n values derived by Hoefnagle and Wepster σ^+ values of Brown Okamoto.

Table.2.Values of σ^n and σ^+ for para substituents

Substituent	σ^n	σ^+
F	+0.15	-0.08
Cl	+0.26	+0.11
Br	+0.28	+0.14
I	+0.30	+0.13
CH ₃	-0.12	-0.32
OCH ₃	-0.13	-0.79

The constants, ρ is a reaction parameter dependent on the nature of the reaction, solvent and temperature, and is a measure of the susceptibility of the reaction centre to the influence of substituents. In the Table 3 are presented some reaction and their Hammett reaction constants.

Table.3.Reaction constants (ρ -values)

Reaction	ρ
Ionisation, ArCOOH, in water at 25 ⁰ C	+1.000
Ionisation, ArCH=CHCOOH, in water at 25 ⁰ C	+0.466
Ionisation, ArC ₆ H ₄ COOH, in water at 25 ⁰ C	+0.370
Ionisation, ArSH, in 95% alcohol at 20-22 ⁰ C	+2.847
Saponification, ArCOOC ₂ H ₅ , in 85% ethanol at 25 ⁰ C	+2.537
Solvolysis, ArCH ₂ Cl, in 50% acetone at 60 ⁰ C	-1.688
Quaternisation, ArN(CH ₃) ₂ , in 90% acetone at 35 ⁰ C	-3.306

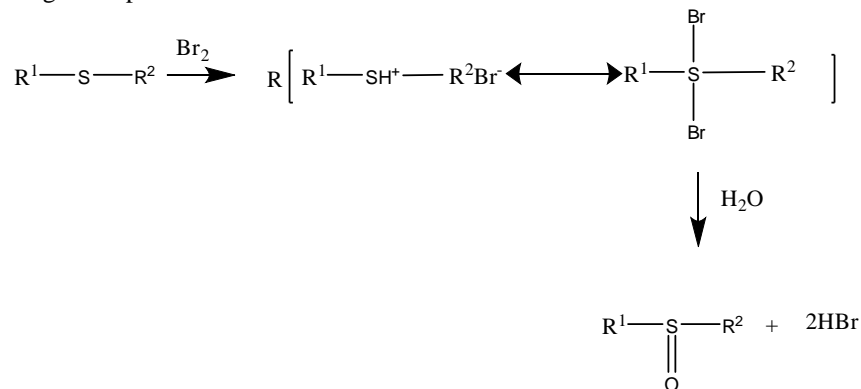
Kinetics and mechanism of oxidation of sulfides:

Importance of Sulfur compounds: Organosulfur compounds such as sulfoxides and sulfones are useful synthetic reagents in organic chemistry. In particular sulfoxides are important intermediates in the synthesis of natural products and drugs and biologically significant molecules. They have also been employed as ligands in asymmetric catalysis and as oxo-transfer reagents. Recent reviews are also there for the synthesis and utilization of chiral sulfoxides are important synthetic intermediates in the preparation of biological and medicinal compounds. Sulfoxides have been also used extensively in C-C bond formation, molecular rearrangements and functional group transformations.

DCICA as selective Oxidant: Dichloroisocyanuric acid, also known Dichloro-s-triazinetriene. It is an oxidizer that reacts with water to form hypochlorous acid, a compound related to the active ingredient in bleach. It is manufactured by chlorination of cyanuric acid:



In the oxidation of sulphides with molecular halogens, it is proposed that halogen form halosulphonium salt with sulphide which subsequently hydrolyse to give sulphoxide.



The kinetics and mechanism of the oxidation of sulphides with N-bromoacetamide (NBA) in the presence of Hg(II) salts suggest that both NBA and the sulphide form complexes with Hg(II) ions and that these complexes participate in the rate-determining step, the formation of a halosulphonium cation, in the rate determining step, which hydrolyses to the sulfoxides. However, addition of Hg (II) was found to be not necessary in the oxidation of sulphides with N-chloroacetamide (NCA).

In the present investigation, kinetics oxidation of arylthioacetic acids by Dichloroisocyanuric acid (DCICA) was carried out, as it was found to be a versatile oxidizing agent and has been used for the oxidation of a variety of organic substrates. Dichloroisocyanuric acid functions mainly as two electron oxidant, though few reactions are known in which it acts as one electron oxidant.

MATERIALS AND METHODS

All the chemicals used in the experiment were of A.R grade. Double distilled water was used for all purposes of the experiment.

Preparation of phenylthioacetic acid:

Thiophenol: The procedure adopted was a modification of the method described by Vogel. A mixture of 240 g of concentrated sulphuric acid and 720 g of crushed ice was taken in a two litre flask. Sixty grams (0.33 mole) of benzenesulphonyl chloride was added to the flask. Zinc dust (120 g, 2 grams atoms) was then added in a few lots, while the contents of the flask were shaken gently. The contents were then steam-distilled. The distillate was extracted with ether and dried over calcium chloride. Removal of ether gave thiophenol which distilled at 169-170°C. The yield was 85%.

Phenylthioacetic acid: To a cold solution of sodium hydroxide (10 ml) was added without allowing the temperature to rise. After that the thiophenol (0.05 mole) prepared by the above method was dissolved in sodium hydroxide (10 ml; 20%) was added to the above solution with cooling and constant shaking. The mixture was then heated in an oil bath at 120-30°C for 5 hrs. The reaction mixture was acidified (50% HCl; congo red) and filtered. The precipitated acid was crystallized from water. The yield of the product was around 70% and the compound melted at 60-61°C. McMillan and Murphy reported the same melting point.

Kinetic measurements:

Kinetics of oxidation of arylthioacetic acids with Dichloroisocyanuric acid:

Purification of materials: The sulphides were purified by crystallization to constant melting point. The samples were dried in vacuum before use.

Acetic acid: Acetic acid (A.R) was refluxed with chromium trioxide for four hours followed by fractional distillation through Dufton column. The fraction boiling at 117-118°C was collected and used.

Other reagents: Dichloromethane was recrystallised from acetic acid before use. All other chemicals used were of A.R. grade. Doubly distilled water was used for all purposes.

Kinetic Procedure: Titrmetric procedure was followed for all kinetic runs. Measurements were made at 30°C, 40°C and 50°C. The temperature was controlled by using a thermostat (accuracy ± 0.1°C). Measurements were made with volumetric glassware calibrated in the usual way. The reaction vessels were blackened from outside to any possible photochemical effect. The medium used was aqueous acetic acid [80:20(v/v)]. The concentration of Dichloroisocyanuric acid solution was determined by iodometric method.

The solution of the arylthioacetic acids were prepared by dissolving the appropriate quantity of the compounds in the same solvent, so that the concentration of the substrate was always maintained greater than the concentration of Dichloroisocyanuric acid

The sulphide solution and Dichloroisocyanuric acid solutions thermally equilibrated. Equal volumes (20 ml) of these solutions were pipetted out into a flask kept in the thermostat. A stop watch was started when half of the Dichloroisocyanuric acid solution had been delivered. 5ml aliquots were quenched into a 0.3N solution (20 ml) of potassium iodide containing 0.3 g of sodium bicarbonate, treated with 6 M sulphuric acid (2 ml), set aside for ten minutes for the complete liberation of iodine, diluted with water (70 ml) and then titrated with a standard solution of sodium thiosulphate using starch as indicator. The sodium thiosulphate solution was standardized by the same procedure using aqueous dichromate solution. The disappearance of blue colour is the end point of the titration. From the titre value, the amount of Dichloroisocyanuric acid reacted was calculated.

Product Analysis: The sulfide solutions were mixed with the oxidizing agents and kept for about twenty four hours. The concentration of the oxidizing agents was kept slightly higher than that of the concentration of sulfide. An analysis of the product revealed that only sulfoxides were isolated and no sulfones could be detected in the reaction mixture. The product obtained was characterized by physical properties.

Stoichiometry: A number of reaction mixtures containing excess of Dichloroisocyanuric acid than sulphide were kept in a thermostat at 30°C for two days. The estimation of the unreacted Dichloroisocyanuric acid indicated that in all cases one mole of Dichloroisocyanuric acid was used for the oxidation of one mole of sulphide.

Calculation of the rate constants: The rate constants were calculated using the second order rate equation:

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

where, 'a' is the initial concentration of substrate in moles/lit., 'b' is the initial concentration of Dichloroisocyanuric acid in moles/lit., 'x' is the amount of Dichloroisocyanuric acid reacted in time t and 't' is the reaction time in seconds. The results of the kinetic runs and rate constants for the oxidation of various compounds and various conditions were incorporated in the results and discussion.

RESULTS AND DISCUSSION

Several studies have been reported on the kinetics of oxidation of organosulphur compounds. Mechanism and rate of oxidation of these compounds was found to be largely affected by the nature of oxidant. The rate constant for the oxidation of some substituted phenylthioacetic acids by DCICA in 80% (v/v) aqueous acetic acid were determined at 30⁰, 40⁰ and 50⁰C.

The rate constants for the oxidation of phenylthioacetic acid by DCICA in 80% (v/v) aqueous acetic acid were determined at 30⁰C. The reaction was found to follow a total second order-first order each in sulphide and DCICA.

Almost all the runs were carried out under the condition of mutual check in order to ensure the constancy of the rate constants. These were believed to be accurate to 2-3% and are reproducible within this limit. A few of the runs separated by many months gave so consistent a value that high reproducibility can be claimed for the whole investigation.

The results of kinetic measurements for meta and para substituted phenylthioacetic acids were carried out under second order conditions at 30⁰C, 40⁰C and 50⁰C and are presented in table.

Table.4. Second order rate constants (K_2), of activation on the oxidation of substituted phenylthioacetic acids by DCICA.

Substituent	$K_2 \times 10^3$		
	30 ⁰ C	40 ⁰ C	50 ⁰ C
H	7.48	13.66	24.24
P-OCH ₃	15.26	27.44	53.62
P-CH ₃	9.46	16.24	29.86
P-Cl	8.88	14.46	21.42
P-Br	7.63	12.78	19.64
P-NO ₂	6.88	11.26	16.82
m-OCH ₃	13.42	21.26	38.44
m-CH ₃	8.52	14.34	27.32
m-Cl	7.48	12.36	19.82
m-Br	6.66	11.20	16.32
m-NO ₂	5.26	9.62	13.70
o-OCH ₃	11.26	16.46	24.42
o-CH ₃	6.84	11.20	18.38
o-Cl	4.48	7.63	9.22
o-Br	3.62	4.80	6.24
o-NO ₂	2.28	3.42	4.62

Qualitatively speaking, electron releasing groups increase the rate and electron withdrawing groups decrease. An analysis of the data may be made from the stand point of the Hammett equation.

CONCLUSION: The DCICA oxidation of Phenylthioacetic acids follows second order rate constant in which DCICA itself is the oxidizing species.

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