Structure-reactivity relation in the oxidation of some aliphatic aldehydes by Tripropylammonium chlorochromate

Jangir Rakesh, Kumawat Ketul, Bishnoi Pramila and Prakash Om*
Chemical Kinetics Laboratories, Department of Chemistry, J.N.V. University, Jodhpur – 342 005 (Rajasthan), INDIA
*drpkvs27@yahoo.com

Abstract

The oxidation of six aliphatic aldehydes by tripropylammonium chlorochromate (TPACC) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is of first order each in TPACC. A Michaelis-Menten type of kinetics is observed with respect to the aldehydes. The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated acetaldehyde MeCDO exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.75$ at 298 K).

The oxidation of acetaldehyde has been studied in nineteen different organic solvents. The solvent effect has been analysed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's σ^* values, reaction constants being negative. A mechanism involving transfer of hydride ion has been suggested.

Keywords: Aldehydes, correlation analysis, halochromate, kinetics, mechanism, oxidation.

Introduction

A large number of halochromates have already been used as mild and selective oxidizing reagents in synthetic organic chemistry[2,4,9,14,24]. Tripropylammonium chlorochromate (TPACC) is also one of such compounds used for the oxidation of primary and secondary alcohols[13]. The kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several studies on halochromates including TPACC have already been reported.[6,21,23,27] In continuation of our earlier work, we report here the kinetics and mechanism of oxidation of six aliphatic aldehydes by TPACC in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are also discussed.

Material and Methods

Materials: TPACC was prepared by the reported method[13] and its purity was checked by iodometric determinations. Solutions of formaldehyde were prepared by heating para-formaldehyde and passing its vapours in DMSO. The amount of HCHO in DMSO was determined by chromotropic acid method[22]. Other aldehydes were commercial products and were used as such. p-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. Deuteriated acetaldehyde (MeCDO) was obtained from Sigma Chemicals. Solvents were purified by their usual methods[26].

Product Analysis: The product analysis was carried out under kinetic conditions. In a typical experiment, acetaldehyde (4.4 g, 0.1mol) and TPACC (2.79 g, 0.01mol) were dissolved in DMSO (100 ml) and the reaction mixture was allowed to stand for *ca*. ≈ 24 to ensure completion of the reaction. It was then rendered alkaline with NaOH, filtered and the filtrate was reduced to dryness under pressure. The residue was acidified with perchloric acid and extracted with diethyl ether (5%, 50 ml). The ether extract was dried ($MgSO_4$) and treated with 10 ml of thionyl chloride. The solvent was allowed to evaporate.

Dry methanol (7 ml) was added and the HCl formed was removed in a current of dry air. The residue was dissolved in diethyl ether (200 ml) and the ester content was determined colorimetrically as Fe (III) hydroxymate by the procedure of Hall and Schaefer[15]. Several determinations indicated a 1:1 stoichiometry. The oxidation state of chromium in a completely reduced reaction mixture determined by iodometric titrations was 3.95 ± 0.1.

Kinetic Measurements: Pseudo-first-order conditions were attained by keeping an excess (×15 or greater) of the [aldehyde] over [TPACC]. The solvent was DMSO unless mentioned otherwise. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions. The reactions were carried out at constant temperature (±0.1 K) and were followed up to 80% of the extent of reaction by monitoring the decrease in [TPACC] at 375 nm. The pseudo-first-order rate constant k_{obs} was computed from the linear least-squares plot of log [TPACC] versus time. Duplicate runs showed that the rate constants were reproducible to within ±3%. The second order rate constant k_2 was calculated from the relation: $k_2 = k_{obs}/[\text{aldehyde}]$.

Results and Discussion

The rate and other experimental data were obtained for all the aldehydes. Since the results are similar, only representative data are reproduced here.

Stoichiometry: The oxidation of aliphatic aldehydes by TPACC leads to the formation of corresponding carboxylic acids. The overall reaction may be written as:

Oxidation Kinetics of some Lower Oxyacids of Phosphorus by Tripropylammonium Chlorochromate: Determination of Reactive Reducing Species

Rakesh Jangid, Ketul Kumawat, Pramila Bishnoi, Ambika Singadiya and Om Prakash*

Chemical Kinetics Laboratory, Department Of Chemistry, J.N.V. University, Jodhpur, 342 005 – (Rajasthan) – India
E-mail: drpkvs27@yahoo.com

Abstract: Oxidation of lower oxyacids of phosphorus by Tripropylammonium chlorochromate (TPACC) in dimethylsuloxide (DMSO) leads to theformation of corresponding oxyacids with phosphorus in a higher oxidation state. The reaction exhibits 1:1 stoichiometry. The reaction is first order with respect to TPACC. A Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction does not induce polymerization of acrylonitrile. Reactions are catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated phosphinic and phenylphosphinic acids exhibited a substantial primary kinetic isotope effect. The oxidation was studied in nineteen different organic solvents. The solvent effects were analysed in terms of Taft's and Swain's multiparametric equations. The effect of solvent indicats the solvent polarity plays a major role in the process. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive reductant and it has been concluded that tricoordinated forms of phosphorus oxyacids does not participate in the oxidation process. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

Keywords: Halochromates, Kinetics, Mechanism, Oxidation, Phosphorus acids. Reducing species

Introduction

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non- aqueous solvents[1-5]. Tripropylammonium chlorochromate (TPACC) is also one of such compounds used for the oxidation of primary and secondary alcohols[6]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several studies on halochromates including that of TPACC, have already reported from our group[7-10]. Further thelower oxyacids are reported to exist in two tautomeric forms[11-12], and it is of interest to determine the nature and species of the oxyacid acid which is involved in the oxidation process. There seems to be no report on the oxidation of oxyacids of phosphorous by TPACC, therefore we report in this article the kinetics of oxidation of phosphinic (PA), phenylphosphinic (PPA) and phosphorous (POA) acids by TPACC in dimethylsulphoxide (DMSO) as a solvent. A suitable mechanism has also been proposed.

Kinetic and mechanistic studies in the Oxidative regeneration of carbonyl compounds from oximes by diethylammonium chlorochromate

Kumawat Ketul[1], Yajurvedi Deeksha[2], Choudhary Anurag[1] and Prakash Om[1]*
1. Chemical Kinetics Lab., Department of Chemistry, J.N.V. University, Jodhpur (Rajasthan), INDIA
2. Department of Chemistry, RG Girls (PG) College, Meerut (U.P.), INDIA
*drpkvs27@yahoo.com

Abstract
The oxidative deoximination of several aldo- and keto-oximes by diethylammonium chlorochromate (DEACC), in dimethylsulphoxide (DMSO) exhibited a first order dependence on DEACC. A Michaelis-Menten type kinetics was observed with respect to oximes. The oxidation of ketoximes is slower than that of aldoximes. The rates of oxidation of aldoximes correlated well in terms of Pavelich-Taft dual substituent-parameter equation. The low positive value of polar reaction constant indicated a nucleophilic attack by a chromate-oxygen on the carbon.

The reaction is subject to steric hindrance by the alkyl groups. The reaction of acetaldoxime has been studied in nineteen different organic solvents. The solvent effect has been analysed by multiparametric equations. A mechanism involving the formation of a cyclic intermediate, in the rate-determining step is suggested.

Keywords: Carbonyl compounds, Dichromates, Kinetics, Mechanism, Oxidation, Oximes.

Introduction

Regeneration of carbonyl compounds from its derivatives under mild conditions is an important process in synthetic organic chemistry. Several oxidative methods are available for deoximation[9]. Salts of Cr(VI) have long been used as oxidizing reagents in synthetic organic chemistry. However, these salts are drastic and non-selective oxidants in nature. Further, they are insoluble in most of the organic solvents also. Thus miscibility is a problem.

To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in synthetic organic syntheses as mild and selective oxidants in non-aqueous solvents[13]. One such compound is diethylammonium chlorochromate (DEACC)[23]. Only a few reports are available in literature regarding oxidation aspects of DEACC[5,17,19].

It is known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. Therefore, in continuation of our earlier work[3,15,18,20,21], we report here the kinetics of the oxidative deoximation of several aldo- and keto-oximes by DEACC in several organic solvents but mainly in dimethylsulphoxide (DMSO). mechanistic aspects have also been discussed.

Material and Methods

Materials: Oximes were prepared by the reported standard methods[24] and their melting points were checked with the literature values. DEACC was prepared by the reported method[23]. Solvents were purified by the usual procedure[17].

Product Analysis: The oxidation of the oximes results in the regeneration of corresponding carbonyl compounds as confirmed by TLC (eluent: CCl_4/Et_2O). Isolation of the product was attempted in the oxidation of oximes of benzaldehyde and acetophenone. In a typical experiment, the oxime (0.2 mol) and DEACC (0.02 mol) were dissolved in 50 ml of DMSO and allowed to stand for *ca*. 10 h for the completion of the reaction. Silica gel (5 g) was then added to the reaction mixture and the mixture was stirred for 15 min[1]. It was then filtered and the solid residue was washed with the solvent (2 % 15 ml).

The solvent was removed on a rotary evaporator and the residue was purified on a silica-gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded the pure carbonyl compound. Yields of benzaldehyde and acetophenone were 1.83 g (86%) and 2.11 g (88%) respectively. The presence of HNO_2 in completely reduced. Reaction mixture was confirmed by a positive starch-iodide test[8]. The oxidation state of chromium in a completely reduced reaction mixture as determined by an iodometric method, is 3.95±0.10.

Kinetics Measurements: The reactions were studied under pseudo-first-order conditions by keeping a large excess (× 10 or greater) of the oxime over DEACC. The solvent was DMSO, unless mentioned otherwise. The reactions were studied at constant temperature (±0.1 K). The reactions were followed by monitoring the decrease in the concentration of DEACC at 352 nm spectrophotometrically. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear least-squares plots of log [DEACC] versus time. Duplicate kinetic runs showed the rate constants to be reproducible to within ±4%.

Results and Discussion

Stoichiometry: The analysis of products indicated the following overall reaction.

Turkish Computational and Theoretical Chemistry

Turkish Comp Theo Chem (TC&TC)

Volume(Issue): 9(1) – Year: 2025 – Pages: 53-62

e-ISSN: 2602-3237

https://doi.org/10.33435/tcandtc.1443581

Received: 27.02.2024 **Accepted:** 23.07.2024 *Research Article*

Correlation Analysis of Structure & Reactivity In The Oxidation of Aromatic Aldehydes By 2-Picolinium Chlorochromate

Ketul Kumawat, Anurag Choudhary[1], Om Prakash

Chemical Kinetics Laboratories, Department of Chemistry, J.N.V. University, Jodhpur (Rajasthan) India

Abstract: Oxidation of thirty-six monosubstituted benzaldehydes by 2-picoliniumchlorochromate (PICC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. A Michaelis-Menten type kinetics was observed with respect to the reactants. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form $k_{obs}= a + b [H^+]$. The oxidation of [^{2}H] benzaldehyde (PhCDO) exhibited a substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the effect of solvent was analysed using Taft's and Swain's multi-parametric equations. The rates of the oxidation of para- and meta-substituted benzaldehydes showed excellent correlation in terms of Charton's tri-parametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes was correlated well with tetra-perametric LDRS equation. The oxidation of para-substituted benzaldehydes is more susceptible to the delocalized effect than is the oxidation of ortho- and meta- substituted compounds, which display a greater dependence on the field effect. The positive value of η suggests the presence of an electron-deficient reaction centre in the rate-determining step (r.d.s.). The reaction is subjected to steric acceleration by the ortho-substituents. A suitable mechanism has been proposed.

Keywords: Benzaldehydes, Correlation, Halochromate, Mechanism, Oxidation

1. Introduction

Halochromates have been used as slow and selective oxidizing reagents in synthetic organic chemistry **[1-5]**. 2-picolinium chlorochromate (PICC) is also one of such compounds used as mild and selective oxidizing agent in synthetic organic chemistry **[6]**. We have been interested in kinetics of oxidations by Cr (VI) species and have already published a few reports on oxidation by other pyridinium **[7,8]** and quinolinium halochromates **[9,10]**. In continuation of our earlier work, we report in the present article the kinetics of oxidation of some mono-substituted benzaldehydes by PICC in DMSO as solvent. The major objective of this investigation was to study the structure -reactivity correlation for the substrate undergoing oxidation.

2. Method

2.1. Materials and Methods

PICC was prepared by reported method **[6]** and its purity was checked by iodometric method. The aldehydes were commercial products. The liquid aldehydes were purified through their bisulfite addition compounds and distilling them, under nitrogen, just before use **[11]**. The solid aldehydes were recrystallized from ethanol. Deuteriated benzaldehyde (PhCDO) was also prepared by the reported method **[12]**. Its isotopic purity, as ascertained by its NMR spectrum, was 96±5%. Due to non-aqueous nature of the solvent, toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual methods.

[1] Corresponding Authors

e-mail: anurag051981@gmail.com

Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2025, 14 (2): 207-216

(International Peer Reviewed Journal)

Structure-Reactivity Correlation in the Oxidation of Aliphatic Primary Alcohols by Tripropylammonium chlorochromate

Pramila Bishnoi, Ambika Singadiya, Rakesh Jangir, Ketul Kumawat and Om Prakash*

Chemical Kinetics Laboratory, Department of Chemistry, J.N.V. University, Jodhpur (Rajasthan), **INDIA**

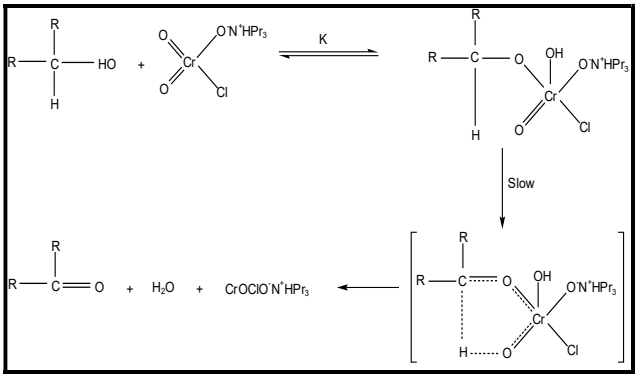
Email: drpkvs27@yahoo.com

Accepted on 4th March, 2025

ABSTRACT

The oxidation of nine aliphatic primary alcohols by Tripropylammonium chlorochromate (TPACC) in dimethylsulfoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to TPACC. A Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form $k_{obs} = a + b[H^+]$. The oxidation of [1,1-$^2H_2$]ethanol ($MeCD_2OH$) exhibits a substantial primary kinetic isotope effect (k_H/k_D = 5.60 at 298K). The reaction has been studied in nineteen different organic solvents. The solvent effect was analysed using Taft's and Swain's multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed.

Graphical abstract:



Acid Independent Path

Keywords: Correlation analysis, Halochromates, Kinetics, Mechanism, Oxidation.

INTRODUCTION

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However, these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus, miscibility is a problem. To overcome these limitations, a largenumber of organic derivatives of Cr(VI)

JCBPS; Section A;February2025 to April2025, Vol. 15, No. 2; 156-164.E- ISSN: 2249 –1929
[DOI: 10.24214/jcbps.A.15.2.15664]

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

International scientific indexing (ISI) Impact Factor (2024-2025) 03.362

*Available online at*www.jcbsc.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT Research Article

Oxidation Kinetics of DL-Methionine, a Sulphur containing Amino acid by Tripropylammonium Chlorochromate

Ambika Singadiya, Rakesh Jangir, Pramila Bishnoi, Ketul Kumawat and Om Prakash*

Chemical Kinetics Lab., Department of Chemistry, J.N.V. University, Jodhpur (Rajasthan) India

Received: 24February 2025; **Revised:** 14March 2025; **Accepted:** 25 March 2025

Abstract: The oxidation of methionine (Met) by tripropylammonium chlororochromate (TPACC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding sulphoxide. The reaction is of first order with respect to TPACC. Michaelis-Menten type kinetics was observed with respect to methionine. The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the form: k_{obs} = a + b [H^+]. The oxidation of methionine was studied in nineteen different organic solvents. The solvent effect was analyzed by Kamlet's and Swain's multiparametric equations. Solvent effect indicated the importance of the cation-solvating power of the solvent. A suitable mechanism has also been postulated.

Keywords: Halochromate, Kinetics, Mechanism, Methionine, Oxidation.

1.INTRODUCTION

Cr(VI) salts of have long been used as oxidizing reagents in synthetic organic chemistry. However these salts are rather drastic in nature and non-selective oxidants. Further, they are insoluble in most of the organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1]. One of such compounds is tripropylammonium chlorochromate (TPACC) reported by Firozabadi *et al.*[2]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr(VI) and several studies have already been

JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

OXIDATION STUDIES OF SOME PHOSPHORUS OXYACIDS BY TRIPROPYLAMMONIUM CHLOROCHROMATE: ESTABLISHMENT OF REACTIVE REDUCING SPECIES

[1]Rakesh Jangid, [2]Ambika Singadiya [3]Pramila Bishnoi, [4]Ketul Kumawat, and [5*]Om Prakash
[1]Research Scholar, [2]Research Scholar, [3]Research Scholar, [4]CSIR-SRF, [5]Assistant Professor & Research Supervisor

Chemical Kinetics Laboratory, Department Of Chemistry, J.N.V. University, Jodhpur, 342 005 – (Rajasthan) – India

Abstract: Oxidation of lower oxyacids of phosphorus by Tripropylammonium chlorochromate (TPACC) in dimethylsuloxide (DMSO) leads to the formation of corresponding oxyacids with phosphorus in a higher oxidation state. The reaction exhibits 1:1 stoichiometry. The reaction is first order with respect to TPACC. A Michaelis-Menten type of kinetics was observed with respect to the reductants. The reaction does not induce polymerization of acrylonitrile. Reactions are catalysed by hydrogen ions. The hydrogen-ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of deuteriated phosphinic and phenylphosphinic acids exhibited a substantial primary kinetic isotope effect. The oxidation was studied in nineteen different organic solvents. The solvent effects were analysed in terms of Taft's and Swain's multiparametric equations. The effect of solvent indicats the solvent polarity plays a major role in the process. It has been shown that the pentacoordinated tautomer of the phosphorus oxyacid is the reactive reductant and it has been concluded that tricoordinated forms of phosphorus oxyacids does not participate in the oxidation process. A mechanism involving transfer of a hydride ion in the rate-determining step has been proposed.

Keywords: Halochromates, Kinetics, Mechanism, Oxidation, Phosphorus acids. Reducing species

1. INTRODUCTION:

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1-5]. Tripropylammonium chlorochromate (TPACC) is also one of such compounds used for the oxidation of primary and secondary alcohols[6]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several studies on halochromates including that of TPACC, have already reported from our group[7-10]. Further thelower oxyacids are reported to exist in two tautomeric forms[11-12], and it is of interest to determine the nature and species of the oxyacid acid which is involved in the oxidation process. There seems to be no report on the oxidation of oxyacids of phosphorous by TPACC, therefore we report in this article the kinetics of oxidation of phosphinic (PA), phenylphosphinic (PPA) and phosphorous (POA) acids by TPACC in dimethylsulphoxide (DMSO) as a solvent. A suitable mechanism has also been proposed.

2. EXPERIMENTAL

2.1 Materials:

The phosphorous oxyacids were commercial products and used as received. TPACC was prepared by the reported method [6] and its purity was checked by an iodometric method and melting point determination. Deuteriated phosphinic (DPA) and phosphorus acids (DPOA) were prepared by repeatedly dissolving the acid in deuterium oxide (BARC, 99.4%) and evaporating water and the excess of deuterium oxide *in* vacuo[13]. The isotopic purity of the deuterated PA and POA, as determinedfrom their NMR spectra, was 92±5% and 94±5% respectively. Due to the non-aqueous nature of the medium, toluene-p-sulphonic acid was used as a source of hydrogen ions. TsOH is a strong acids and in non-polar solvents like DMSO, it is likely to be completely ionized. Other solvents were purified by their usual methods.

2.2 Stoichiometry:

The oxidation of lower oxyacids of phosphorus leads to the formation of corresponding oxyacids containing phosphorus in a higher oxidation state. Reaction mixtures were prepared containing a known excess of phosphinic or phosphorous acids. On completion of the reaction, the amount of phosphorous formed in the oxidation of phosphinic acid and the residual reductant in

RNI No. MAHENG/2017/74063
ISSN No. (Print) 2581-5911

Correlation Analysis of Reactivity in the Oxidation of some Vicinal and Non-vicinal Diols by Picolinium Chlorochromate

Sapna Rankawat, Divya Chaudhary, Ketul Kumawat and Om Prakash*
Chemical Kinetics Lab., Department of Chemistry, J.N.V. University, Jodhpur, Rajasthan, India
*** E-mail:** drpkvs27@yahoo.com

Abstract:
The kinetics of oxidation of four vicinal, four non-vicinal diols by picolinium chlorochromate (PICC) have been studied in dimethylsulphoxide (DMSO). The main product of oxidation is the corresponding hydroxycarbonyl compound. The reaction is first order in PICC. Michaelies-Menten type of kinetics is observed with respect to the diols. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of [1,1,2,2-$^2H_4$] ethanediol exhibits a substantial primary kinetic isotope effect (k_H/k_D = 5.76 at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical transition state in the rate-determining step. A suitable mechanism has been proposed.

Keywords: *Correlation analysis, diols, halochromate, kinetics, mechanism, oxidation*

Introduction

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus miscibility is a problem. To overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents[1-5]. One of such compounds is picolinium chlorochromate (PICC), reported by reported method.[6] We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr(VI) and several reports on halochromates have already reported from our laboratory[7-10]. There seems to be no report on the oxidation aspects of diols using picolinium chlorochromate (PICC). Therefore, it was of interest to investigate the kinetics of the oxidation of some vicinal and non-vicinal diols by PICC in DMSO. A suitable mechanism has also been postulated.

Materials and Methods

Materials: The diols (BDH or Fluka) were distilled under reduced pressure before use. PICC was prepared by the reported method[6]. [1,1,2,2-$^2H_4$]Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride[11]. Its isotopic purity,

Chemical Science International Journal

Volume 35, Issue 2, Page 35-50, 2026; Article no.CSIJ.154137
ISSN: 2456-706X
(Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

A Mechanistic and Correlative Study on Sulfide Oxidation by Diethylammonium Chlorochromate

Ketul Kumawat [a++], Ram Bharos Mundel [a++], Om Prakash [a#] and Anurag Choudhary [a#*]

[a] *Department of Chemistry, JNV University, Jodhpur, India.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: https://doi.org/10.9734/CSJI/2026/v35i21024

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://pr.sdiarticle5.com/review-history/154137

Original Research Article

Received: 19/01/2026
Published: 21/03/2026

Abstract

The process of turning organic sulfides into their sulfoxides using diethylammonium chlorochromate (DEACC) occurred at first order concerning DEACC. On the other hand, the reaction shows Michaelis–Menten-type kinetics when it comes to the sulfide substrate. We used both single-parameter and multi-parameter correlation equations to conduct a kinetic study of thirty-four distinct sulfides. Charton's LDR and LDRS equations gave the most accurate correlations for aryl methyl sulphides. The polar regression coefficients were negative in these cases. The rate data for alkyl phenyl sulfides matched up quite well with the Pavelich–Taft equation. Also, the oxidation of methyl phenyl sulfide was studied in nineteen distinct organic solvents. Kamlet–Taft and Swain's multiparametric models were used to look at how the polarity and other properties of the solvent affected the reaction. Based on the kinetic measurements, it has been suggested that a reaction mechanism includes the creation of a sulfurane intermediate during the phase that controls the rate.

[++]*Research Scholar;* [#]*Assistant Professor;*
**Corresponding author: E-mail: anurag051981@gmail.com;*

Cite as: *Kumawat, K., Mundel, R. B., Prakash, O., & Choudhary, A. (2026). A Mechanistic and Correlative Study on Sulfide Oxidation by Diethylammonium Chlorochromate. Chemical Science International Journal, 35(2), 35–50. https://doi.org/10.9734/CSJI/2026/v35i21024*