RESEARCH PAPER

Oxidation of Dibenzalacetone by Cetyltrimethylammonium Bromochromate

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ABSTRACT

In the presence of perchloric acid, the oxidation kinetics of some para-substituted dibenzalacetones (DBA) by cetyltrimethylammonium bromochromate (CTMABC) have been investigated in aqueous acetic acid media. A hydrogen ion catalyzes the reaction, which is first order for both DBA and CTMABC. The Hammett relationship is followed by the rate data. The equivalent chalcone epoxide is the result of oxidation. A plausible mechanism for the reaction of CTMABC with DBA has been postulated based on the kinetic data and product analysis.

Keywords: Bromochromate, Oxidation Kinetics, Dibenzalacetone, CTMABC

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1.Introduction

A wide range of organic molecules have been oxidized using chromium compounds in both aqueous and non-aqueous media.

Chromium compounds, particularly Chromium (VI) reagents may be oxidized in most of the organic functional groups. There is still interest in the creation of more advanced chromium (VI) reagents for the oxidation of organic substrates.[1]

The oxidation of dibenzacetone by different oxidants have been the subject of study by various workers due to the complex behavior of their mode of oxidation due to the formation of chalcone epoxide Product many of which find application in pharmaceutical**,** agrochemical**, and** materials science fields. Chalcone epoxides exhibit cytotoxic effects against various cancer cell lines by interfering with microtubule function or inducing apoptosis. They have demonstrated antibacterial and antifungal properties.These derivatives reduce inflammation by inhibiting enzymes like COX and lipoxygenase.

The present study focuses on the study of kinetics and mechanism of oxidation of *para* substituted dibenzalacetone by CTMABC in aqueous acetic acid media.

Dibenzalacetone serves as an intermediate in organic synthesis. It can be used to prepare various compounds, including other conjugated ketones or enones, which are important in the synthesis of pharmaceuticals, fine chemicals, and agrochemicals. Dibenzalacetone can act as a ligand in coordination complexes with metal ions. Due to its ability to donate electrons from the carbonyl oxygen or conjugated double bonds, it forms complexes with various transition metals. Due to its absorption in the UV-visible region, dibenzalacetone is studied for its photochemical properties. It can be used as a photoinitiator or in studies of conjugated systems' behaviour under light exposure. Dibenzalacetone is commonly used in spectroscopic studies, particularly in UV-visible spectroscopy, to demonstrate the properties of conjugated carbonyl systems.Dibenzalacetone derivatives were organic compounds formed by two active sites that provide a large relocation of π-electrons. They have great polarizability that make them excellent chromophore and draw attention for their biological properties, mainly for their activity against nasopharyngeal, oral, colon, prostate and cervical cancer[2]. Dibenzalacetone, was a ketone compound with potential antibacterial properties, especially against *Escherichia coli*[3] . Dibenzalacetone was commonly used in sunscreens to block harmful UV light from harming the skin[4].

The reaction pathways of dibenzalacetone in natural systems are dominated by redox reactions with soil and sediment constituents. Better understanding of the mechanism of oxidation of such compounds/contaminants to harmless products is the important goal for basic research and industrial applications, hence, the present study.

One of the important tools in deciding the mechanism of reaction is the study of substituent effects and thermodynamic parameters. The isokinetic relationship is also an important tool for deciding the nature of a mechanism. Keeping this in view, a systematic study has been made to establish the reactiv-ity and to decide the nature of the mechanism followed in the oxidation of several *para*-substituted dibenzalacetone by CTMABC.

Kinetics of oxidation of dibenzalacetone by various oxidizing reagents have been well studied.[5-13] However the kinetics of oxidation of substituted dibenzalcetone by CTMABC, a Cr(VI) reagent has not yet been studied. Hence, we have considered it worthwhile to study the kinetics and mechanism of oxidation of dibenzalacetone by CTMABC.

2.Experimental

2.1.Materials and reagents

All the chemicals and solvents used were of analytical grade. The dibenzacetone used were with substituents H, p-OCH_3, p-CH_3, p-Cl and p-NO_2. Acetic acid was purified by the standard method and the fraction distilling at 118 °C was collected. Double distilled water was used for all purposes.

2.2 Preparation Of Cetyl Tri Methyl Ammonium Bromo Chromate, $C_{19}H_{42}NCRO_3Br$, CTMABC[14:]

A stoichiometric amount of cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}(CH_3)_3\ N^+\ Br^-$ (3.89 g, 10.7 mmol), is added to a polyethylene beaker containing a measured amount of chromium(VI) oxide (CrO_3: 1.07 g, 10.7 mmol) that has been dissolved in dry acetonitrile (25 ml) inside an argon-purged glove box. The mixture is stirred at room temperature. A clear orange solution is produced in five minutes. Solid CTMABC develops in the refrigerator and is

separated by filtering, washing with dry isopropanol and diethyl ether, pressing between filter paper folds, and vacuum-drying for one hour. After a week, the concentrated solution of $CH_3(CH_2)_{15}$ $N^+(CH_3)_3$ $[CrO_3Br]^-$ in acetonitrile slowly evaporates to produce the right crystals.
Production Yield:4.71 g (95%);
Melting point 104°C.

2.3 Elemental analysis of CTMABC:

Elemental analysis of CTMABC carried out by a CHN analyser. It gives C, H, and N values. O is typically calculated by difference. Bromine and chromium content is typically determined by titrimetric methods. Elemental analysis confirms the presence of elements like C, H, N, Br, Cr and O, and matches the **empirical formula** of the compound. For the base compound, $C_{19}H_{42}BrCrNO_3$ (Molecular Weight = 478.46 g/mol):

Carbon (C)	~47.7%
Hydrogen (H)	~8.9%
Nitrogen (N)	~2.9%
Bromine (Br)	~16.7%
Chromium (Cr)	~10.8%
Oxygen (O)	~10.1%

Further analayse, the synthesized Cetyltrimethylammonium Bromochromate has studied in spectral characterization like

1. FT-IR spectroscopy
2. UV-visible spectroscopy
3. H^1 NMR spectroscopy and
4. C^{13} NMR spectroscopy

2.3 Spectral Characterization of Cetyltrimethylammonium Bromochromate :

The FT-IR spectrum of Cetyltrimethylammonium Bromochromate was obtained using the BRUKER ALPHAFT-IR MB 102 spectrophotometer, in the 4000-400 cm^{-1} region on KBr pellets. The electronic spectra (UV-Vis spectra) of Cetyltrimethylammonium Bromochromate was put on record in ethanol solvent using UV-Vis Double Beam Lamda 25 Perkin Elmer spectrophotometer. The ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were performed on the BRUKER ADVANCE spectrometer, using $CDCl_3$

2.4 FT-IR Spectrum of Cetyltrimethylammonium Bromochromate

The Infrared (IR) spectrum of Cetyltrimethylammonium Bromochromate (Figure -1) exhibits characteristic absorption bands corresponding to its functional groups[15]. In figure 1 the peak 2850–2950 cm^{-1}: explained the C–H stretching vibrations from the alkyl chains. In peak 1445 cm^{-1} and 1385 cm^{-1} shows the C–H bending vibrations. The peak 922–1255 cm^{-1} indicates C–N stretching vibration of the quaternary ammonium group. The peak 922 cm^{-1} appears Cr=O stretching vibration and a peak 595–751 cm^{-1}: indicates Cr–O–Br and Cr–O stretching vibrations.

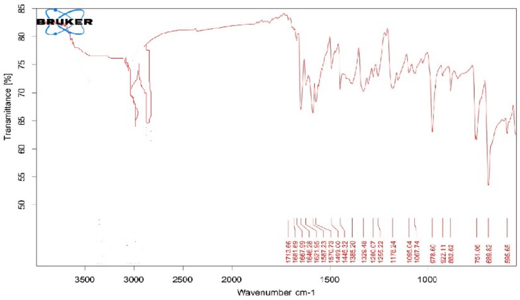


Figure 1: Infra Red Spectrum of Cetyltrimethylammonium Bromochromate

2.5 UV-Visible Spectrum of compound Cetyltrimethylammonium Bromochromate:[16]

With the help of oxygen and bromide ligands, chromium in the +6 oxidation state is present in the bromochromate anion. According to figure 2, ligand-to-metal charge transfer (LMCT) transitions, in which electrons are moved from oxygen ligands to the chromium core, are the cause of the absorption peak at 350 nm. The yellow-orange hue of the molecule is caused by these transitions, which are typical of Cr(VI) compounds. The bromochromate anion is mostly responsible for the observed spectrum because the cetyltrimethylammonium cation does not absorb in the UV–Vis range.

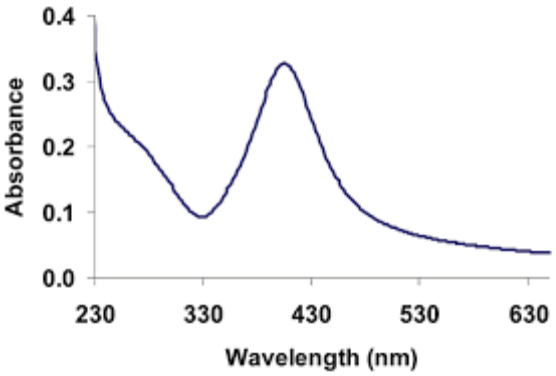


Figure 2: UV Spectrum of Cetyltrimethylammonium Bromochromate

2.6 H^1NMR Spectrum of Cetyltrimethylammonium Bromochromate

In Figure 3 have been explained the H^1 NMR spectrum of synthesized Cetyltrimethylammonium Bromochromate [17] The singlet peak at 3.31 ppm appears the nine protons from the $N^+(CH_3)_3$. _A triplet peak at 3.35 ppm explained the two protons from $CH_2–N^+$. A singlet peak at 1.30 ppm investigated the methylene protons in the long alkyl chain. A triplet peak shows that at 0.95 ppm for the terminal methyl group.

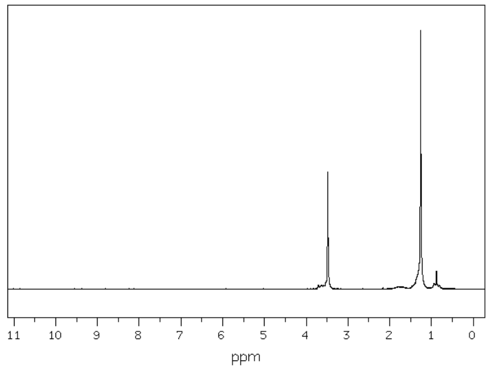


Figure -3 H^1NMR Spectrum of Cetyltrimethylammonium Bromochromate

2.7 C^{13} NMR Spectrum of Cetyltrimethylammonium Bromochromate

In Figure 4 have been explained the C13 NMR spectrum of synthesized Cetyltrimethylammonium Bromochromate [18]

The CTA^+ cation consists of a long alkyl chain (16 carbons) attached to a quaternary ammonium group. The expected chemical shifts in the ^{13}C NMR spectrum are:

The peak 14 ppm shows that the methyl carbon at the end of the alkyl chain) group(terminal CH_3). The peak 30 ppm indicates that the methylene chain carbons($(CH_2)n$). The peak 54 ppm explained the Trimethylammonium methyl carbons($N^+(CH_3)_3$) and the peak 60 ppm investigated the α-methylene carbon ($N^+–CH_2–$).

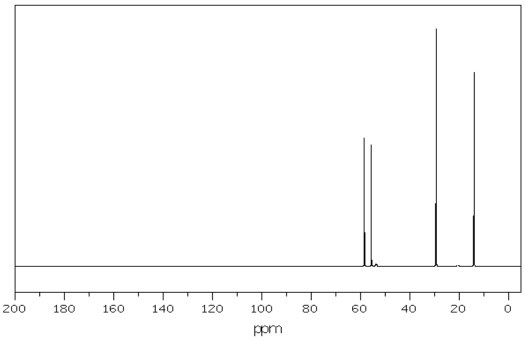
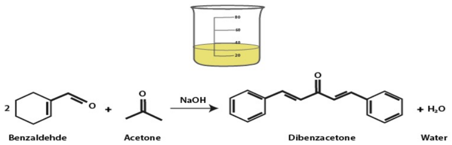


Figure -4 C^{13} NMR Spectrum of Cetyltrimethylammonium Bromochromate

2.8 Preparation of Dibenzalacetone:[4]

A cold solution of 8 g of sodium hydroxide in 250 ml of water and 70 ml of ethanol was placed in a 500 ml round bottom flask equipped with mechanical stirrer and it was surrounded by ice water bath. The temperature of the solution was maintained at 20-25 ºC and stirred vigorously. To the above solution one half of previously prepared mixture (8.8 g of pure benzaldehyde and 2.4 g of acetone) was added. A flocculant precipitate was formed in 2-3 minutes. The remaining portion of benzaldehyde - acetone mixture was added after 15 min. The precipitate was filtered off and washed well with cold water to eliminate the alkali as completely as possible. The solid was dried at room temperature to constant weight and 9 g of crude dibenzalacetone (93%) with m.p. 105-108 ºC were obtained. It was recrystallised from ethyl acetate. The compound melted at 107 ºC [m.p. 105-108 ºC].



Preparation of some para substituted Dibenzalacetone:

p-OCH_3, p-CH_3, p-Cl and p-NO_2 substituted Dibenzalacetones were prepared same method. These compounds were characterized by elemental analysis, IR , UV and NMR spectral Studies

2.9 Elemental analysis of Dibenzalacetone:

Elemental analysis of dibenzalacetone carried out by a CHN analyzer, the DBA sample is combusted, and the percentages of C, H, and O are determined. For dibenzalacetone:Only C and H are directly measured. O is typically calculated by difference. Elemental analysis confirms the presence of elements like C, H, and O**, and** matches the empirical formula of the compound.

For the base compound, $C_{17}H_{14}O$ (Molecular Weight = 234.29 g/mol):

Carbon (C) **):** ~ 87.15%

Hydrogen (H) **):** ~ 6.02%

Oxygen (O) **):** ~ 6.83%

Beyond the synthesized Dibenzalacetone was characterized by the following analytical assays, FT-IR Spectroscopy, UV-Visible Spectroscopy, H^1 NMR Spectroscopy and C^{13} NMR Spectroscopy

2.10. Spectral Characterization of Dibenzalacetone :

The FT-IR spectrum of dibenzalacetone was obtained using the BRUKER ALPHAFT-IR MB 102 spectrophotometer, in the 4000-400 cm^{-1} region on KBr pellets. The electronic spectra (UV-Vis spectra) of Dibenzalacetone was put on record in ethanol solvent using UV-Vis Double Beam Lamda 25 Perkin Elmer spectrophotometer. The ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were performed on the BRUKER ADVANCE spectrometer, using $CDCl_3$

2.11. FT-IR Spectrum of Dibenzalacetone

The Infrared (IR) spectrum of dibenzalacetone(Figure -1) exhibits characteristic absorption bands corresponding to its functional groups[15].Aromatic C-H stretching vibrations are observed at approximately 3023 cm^{-1}.The stretching vibration of the carbonyl group (C=O) appears as a peak around 1681 cm^{-1}. The absorption band at 1493 cm^{-1} corresponds to the stretching vibration of $-CH_2-$ groups.(Table -1)

Table 1 : IR spectral data of DBA

Functional groups	**IR Frequency Cm^{-1}**
Aromatic C-H	3023
C=O	1681
$-CH_2-$	1493

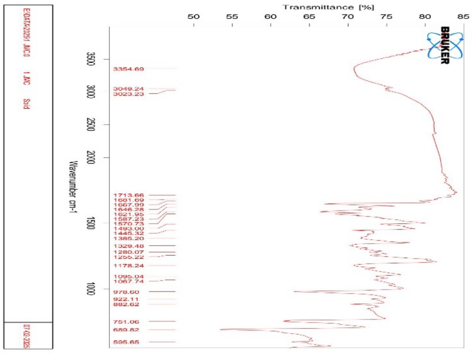


Figure 5: FT-IR Spectrum of Dibenzalacetone

2.12. UV-Visible Spectrum of compound DBA:

In UV-Visible spectroscopy spectrum shows(Figure-2) absorption peaks at **335 nm** and **206 nm**, this suggests the presence of specific electronic transitions[16], likely due to conjugated systems or functional groups in the dibenzalacetone.

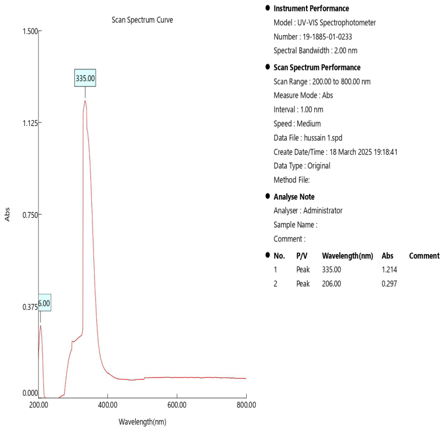
Peak in 335 nm:

- **Region:** Falls in the near-UV to visible range.
- **Possible Transitions:** Typically corresponds to $\pi \rightarrow \pi^*$ transitions.
- **Possible Compounds:**
  - **Conjugated systems**: Molecules with extended conjugation (e.g., polyenes, aromatic rings with electron-donating groups).
  - **Aromatic compounds**: Some substituted benzene derivatives, polycyclic aromatic hydrocarbons (PAHs).
  - **Chromophores like flavonoids** or some organic dyes.
  - **Transition metal complexes** (ligand-to-metal charge transfer).

Peak in 206 nm:

- **Region:** Falls in the deep-UV region.
- **Possible Transitions:** Usually corresponds to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions.
- **Possible Compounds:**
  - **Benzene and substituted aromatics**: Aromatic hydrocarbons typically absorb around 200–210 nm.
  - **Alkenes and conjugated dienes**: Simple alkenes absorb in this range.

- **Proteins and peptides**: Due to peptide bond absorption.
- **Nucleic acids (DNA/RNA)**: Strong absorption due to the purine and pyrimidine bases.



- **Instrument Performance**
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  Number : 19-1885-01-0233
  Spectral Bandwidth : 2.00 nm
- **Scan Spectrum Performance**
  Scan Range : 200.00 to 800.00 nm
  Measure Mode : Abs
  Interval : 1.00 nm
  Speed : Medium
  Data File : hussain 1.spd
  Create Date/Time : 18 March 2025 19:18:41
  Data Type : Original
  Method File:
- **Analyse Note**
  Analyser : Administrator
  Sample Name :
  Comment :

No.	**P/V**	**Wavelength(nm)**	**Abs**	**Comment**
1	Peak	335.00	1.214	
2	Peak	206.00	0.297	

Figure 6: UV-Visible Spectrum of Dibenzalacetone

2.13. H^1NMR Spectrum of DBA

The synthesized dibenzalacetone are characterized by H^1 NMR Spectrum[17](Figure-3) . The Interpretation of this compound is given below(Table -2)

Table 2: H^1 NMR Data of DBA

Proton Type	**Chemical Shift (ppm) Range**
Aromatic Protons	7.09 - 7.79
Alpha-Carbon Proton (adjacent to carbonyl group)	2.40
Methylene Protons	TBD
Aliphatic Protons	TBD

Aromatic Protons : A prominent multiplet in this range was observed, attributed to the aromatic protons on the benzene rings. The signals appeared broadened due to coupling with neighbouring protons. The exact chemical shifts within this range may vary depending on factors such as solvent polarity and ring substitution patterns.

Alpha-Carbon Proton Adjacent to Carbonyl Group : A multiplet centered around δ 2.40 ppm was observed, corresponding to the proton on the alpha-carbon adjacent to the carbonyl group. This multiplet arises due to coupling with neighbouring protons, including those on the benzene rings and neighbouring methylene groups. The chemical shift and splitting pattern provide insights into the chemical environment and connectivity of this proton.

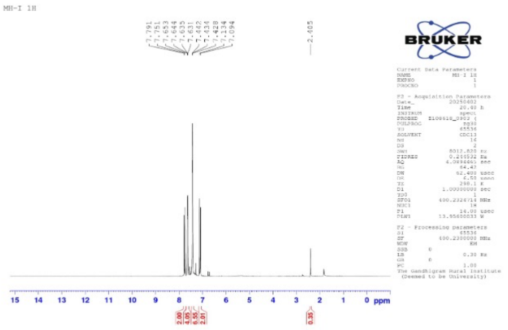


Figure 7: H^1 NMR Spectrum of Dibenzalacetone

2.14. C^{13} NMR Spectrum of DBA

The Synthesized Dibenzalacetone are characterized by C^{13} NMR Spectrum[18].(Figure -4) The Interpretation of this compound is given below.(Table-3)

Table 3: C^{13} NMR Data of DBA

Carbon Type	**Chemical Shift (ppm) Range**
Carbonyl Carbon (C=O)	189
Aromatic Carbons	125 – 143
Aliphatic Carbons	76 – 77

Carbonyl Carbon (C=O) : A sharp peak was observed in the spectrum around δ 189 ppm, corresponding to the carbonyl carbon (C=O) of the molecule. The precise chemical shift of this peak depends on factors such as molecular environment and any conjugation effects with adjacent functional groups.

Aromatic Carbons : Several peaks were observed in the range of δ 125 – 143 ppm, indicative of the carbon atoms within the benzene rings of dibenzalacetone. The chemical shifts of these peaks vary depending on the degree of substitution and the presence of electron-withdrawing or electron-donating groups.

Aliphatic Carbons : Signals corresponding to aliphatic carbons, including those in the alkene and alkyl chains, were observed in the spectrum within the range of δ 0 - 80 ppm. The alpha-carbon adjacent to the carbonyl group may appear around δ 76 - 77 ppm due to the electron-withdrawing effect of the carbonyl group.

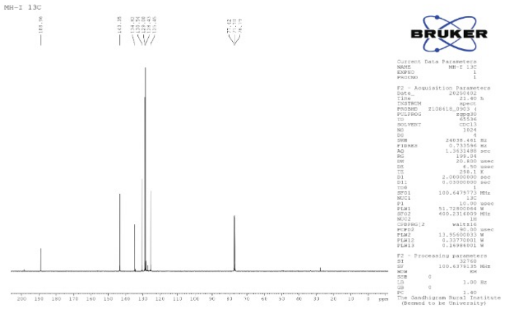


Figure: 8 C^{13}NMR Spectrum of DBA

2.15. Kinetic measurements

By maintaining an excess of substrate over CTMABC, the reactions were conducted under pseudo-first-order conditions.A steady temperature of ±0.1 K was maintained.

Iodometric estimation of the unreacted oxidant at 298, 303, 308, and 313 K for up to 80% of the reaction was used to track the reaction's progress. The linear plots of log [CTMABC] vs time were used to calculate the pseudo-first-order rate constants, or kobs. The rate constants were repeatable to within ± 4%, according to duplicate kinetic runs.

2.16.Data analysis

The computer software Microcal Origin (Version 6.1) was used to do correlation analysis.

The correlation coefficients and standard deviations are used to discuss the fit's quality.

2.17.Stoichiometry and product analysis

Several sets of tests were conducted with different concentrations of CTMABC that were significantly more than DBA in order to ascertain the reaction's stoichiometry. One mol of CTMABC interacts with one mol of DBA, according to the estimation of unreacted CTMABC. Preparative TLC on silica gel, which produces chalcone epoxide.

Melting point of chalcone epoxide: 101 °C

2.18.Elemental analysis of Chalcone epoxide:

Elemental analysis confirms the presence of elements like C, H, and O, and matches the empirical formula of the compound.

Elemental analysis of chalcone epoxide carried out by a CHN analyzer, the chalcone epoxide sample is combusted, and the percentages of C, H, and O are determined. For dibenzalacetone:Only C and H are directly measured. O is typically calculated by difference. Elemental analysis confirms the presence of elements like C, H, and O, and matches the empirical formula of the compound.

For the base compound, $C_{15}H_{12}O_2$ (Molecular Weight = 224.25 g/mol):

- Carbon (C): ~80.34%
- Hydrogen (H): ~5.39%
- Oxygen (O): ~14.29%

Further analyze the chalcone epoxide product was used to characterized by IR spectroscopy,UV spectroscopy, H^1 NMR Spectroscopy and C^{13} NMR spectroscopy.

2.19. Spectral Characterization of Chalcone epoxide :

The FT-IR spectrum of chalcone epoxide was obtained using the BRUKER ALPHAFT-IR MB 102 spectrophotometer, in the 4000-400 cm^{-1} region on KBr pellets. The electronic spectra (UV-Vis spectra) of chalcone epoxide was put on record in ethanol solvent using UV-Vis Double Beam Lamda 25 Perkin Elmer spectrophotometer. The ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were performed on the BRUKER ADVANCE spectrometer, using $CDCl_3$

2.20. IR Spectrum of Chalcone Epoxide:

The infrared spectrum of chalcone epoxide (Figure 9) shows the peak 1700 cm^{-1} explained the C=O stretching of a significant absorption that is characteristic of ketone functional group.[15]The peaks 1250–1270 cm^{-1} and 850–950 cm^{-1}shows epoxide ring vibrations of C–O–C stretches and ring deformations.

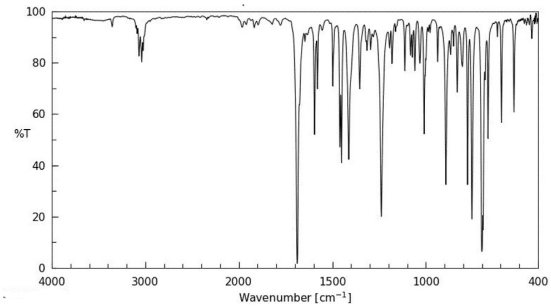


Figure: 9 IR Spectrum of Chalcone epoxide

2.21. UV Spectrum of Chalcone epoxide:

In Figure 10 explained the UV spectrum of Chalcone epoxide. Its exhibit absorption bands in the UV region, primarily due to π→π* electronic transitions associated with aromatic systems.[16]

The absorption band 220–270 nm, attributed to π→π* transitions of the aromatic rings. The absorption band appears around 340–390 nm, also due to π→π* transitions, influenced by the conjugation between the aromatic rings and the carbonyl group.

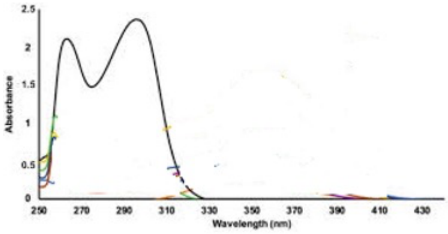


Figure: 10 UV Spectrum of Chalcone epoxide

2.22. H^1 NMR Spectrum of Chalcone epoxide:

The H^1 NMR spectrum of chalcone epoxide (Figure 11) shows the peak multiplets between 7.2–8.0 ppm, corresponding to the ten protons of the two phenyl rings due to aromatic protons. [17]Signals around 4.13 and 4.34 ppm, indicative of the diastereotopic methine protons on the three-membered epoxide ring due to **epoxide ring protons.**

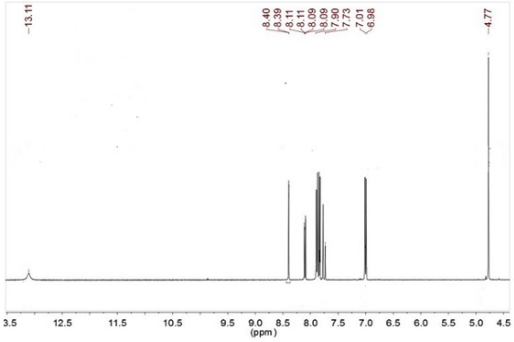


Figure -11 H^1 NMR Spectrum of chalcone epoxide:

2.23. C^{13} NMR Spectrum of Chalcone Epoxide:

In Figure 12 explained the ^{13}C NMR spectrum of chalcone epoxide.

The signal 190–200 ppm explains the carbonyl carbon (C=O). The signal 125–140 ppm shows to the corresponding aromatic carbons and the signals 45–60 ppm range, corresponds to the characteristic of the strained three-membered epoxide ring carbons.[18]

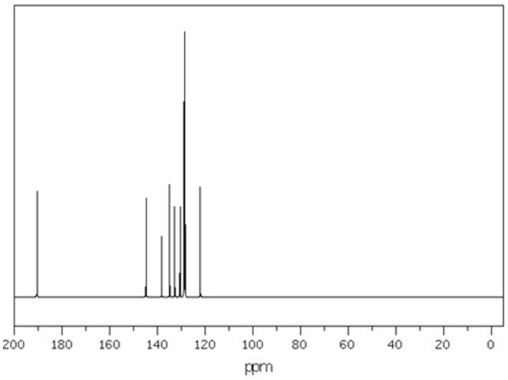


Figure -12 C^{13} NMR Spectrum of Chalcone Epoxide:

3.Results and Discussion

Under pseudo-first-order circumstances, the kinetics of DBA oxidation by CTMABC was investigated at 303 K in a 50% acetic acid—50% water medium. Table 4 lists the observed pseudo-first-order rate constants (k_{obs}).

3.1 Order of the reaction

It was discovered that the oxidation rates in [CTMABC] and [Substrate] were both first order. The first-order dependence of the rate on [Substrate] is shown by linear plots of log k1 versus log [Substrate] (Figure. 13) with unit slope (H: slope = 1.03 ± 0.04, r = 0.997; p-OCH3: slope = 1.02 ± 0.03, r = 0.998; p-CH3: slope = 1.01 ± 0.03, r = 0.999; p-Cl: slope = 1.04 ± 0.04, r = 0.997; and p-NO2: slope = 1.01 ± 0.03, r = 0.998).

Table 4 lists the k1 values at various [Substrate]. The k_1 values acquired at various CTMABC concentrations show that the rates are mostly unaffected by the starting CTMABC concentration. This ensures that the reaction's order with respect to CTMABC is one.

At various starting concentrations and while maintaining the concentrations of the other reactants constant, the relationship between the reaction rate and the hydrogen ion concentration has been examined (Table 4). It is evident that when the concentration of hydrogen ions rises, the rate of reaction increases linearly. This proves that, in relation to the concentration of hydrogen ions, the reaction rate is first order. The linear plot of log k_1 against log $[H^+]$ in Figure 14 indicates that the reaction proceeds entirely via an acid-catalyzed route.[19-20]

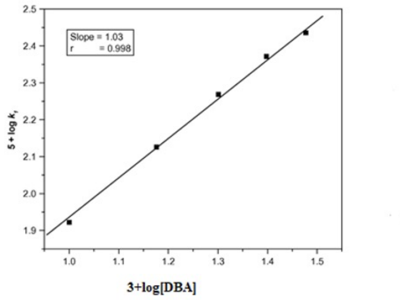


Figure 13 Plot of log k_1 versus log [DBA] for the oxidation of DBA by CTMABC

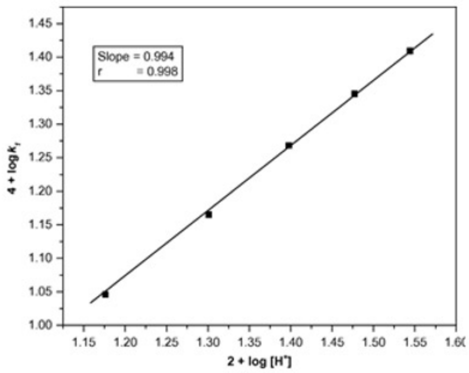


Figure 14 Plot of log k_1 versus log $[H^+]$ for the oxidation of DBA by CTMABC

Table 4 Effect of variation of [DBA], [CTMABC] and $[H^+]$ on the rate of reaction at 303 K.

Solvent composition= 50% AcOH – 50% H_2O (v/v).

a Contained 0.001 mol dm^{-3} acrylonitrile.

b In the presence of 0.003 mol dm^{-3} Mn(II).

10^3 [CTMABC] (mol dm^{-3})	10^2 [DBA] (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	10^4 k_1 (s^{-1})				
			H	*p*-OCH$_3$	*p*-CH$_3$		*p*-NO$_2$
0.5	2.0	0.25	18.46	26.20	22.70	10.42	3.62
1.0	2.0	0.25	18.56	26.40	22.40	10.56	3.60
1.5	2.0	0.25	18.44	26.34	22.20	10.30	3.48
2.0	2.0	0.25	8.42	26.56	22.10	10.12	3.56
2.5	2.0	0.25	18.32	26.12	22.96	10.52	3.70
1.0	1.0	0.25	8.96	12.80	10.88	5.12	1.76
1.0	1.5	0.25	13.36	19.20	16.48	7.68	2.72
1.0	2.5	0.25	23.52	32.96	27.20	12.64	4.48
1.0	3.0	0.25	27.28	39.84	33.60	15.20	5.28
1.0	2.0	0.15	11.12	15.44	13.22	6.28	2.08
1.0	2.0	0.20	14.64	21.02	17.66	8.40	2.78
1.0	2.0	0.30	22.16	31.28	26.42	12.56	4.28
1.0	2.0	0.35	25.68	36.70	30.66	14.66	4.92
1.0	2.0	0.25	18.48	26.32	22.46	10.48	3.65^a
1.0	2.0	0.25	15.22	21.12	18.36	8.76	2.94^b

3.2 Effect of varying solvent composition:

By changing the acetic acid content from 30%

to 70%, the impact of solvent composition on the reaction rate was investigated. All of the substituted dibenzalacetone's oxidation processes were estimated to have pseudo-first-order rate constants using CTMABC at constant ionic strength in the presence of perchloric acid. As the amount of acetic acid in the medium increases, the reaction rate rises noticeably (Table 5).

While the dielectric constant of the medium decreases, the acidity of the medium increases as the acid concentration of the media increases. The rate of oxidation increases significantly as a result of these two processes. Two causes may often be ascribed to the augmentation of the reaction rate with an increase in the quantity of acetic acid: (i) the rise in acidity at constant [H+] and (ii) the decrease in the dielectric constant with an increase in the acetic acid content. An interaction between a positive ion and a dipolar molecule is shown by the linear, positive-sloped plots of log k1 versus the inverse of the dielectric constant. [19-20]

Table 5 Effect of varying solvent polarity on the rate of reaction at 303 K.

[DBA] = 2.0 X 10^{2} mol dm^{-3} [CTMABC] = 1.0 X 10^{3} mol dm^{-3}
$[H^{+}]$ = 2.5 X 10^{-1} mol dm^{-3}

%Acetic acid–water (v/v)	Dielectric constant	10^{4} k_1 (s^{-1})				
		H	*p*-OCH_3	*p*-CH_3	*p*-Cl	*p*-NO_2
30–70	72.0	13.46	20.90	18.02	6.66	2.34
40–60	63.3	15.30	23.76	21.16	8.56	3.02
50–50	56.0	18.56	26.40	22.40	10.56	3.60
60–40	45.5	20.96	29.58	25.26	12.96	4.32
70–30	38.5	23.47	33.12	28.41	14.51	4.85

Despite being surprisingly sluggish, the oxidation of DBA by CTMABC in an acetic acid water medium is catalyzed by perchloric acid and occurs at a comfortable pace. Perchloric acid catalysis implies that CTMABC species, not the DBA molecule, are protonated, which would have caused retardation. Although protonated CTMABC is hard to see, protonated chromium (VI) oxidation is recognized to have a role[21]. There were no free radicals present because the reaction did not encourage the polymerization of acrylonitrile.

The loss of the hydride ion is followed by the development of a complex as the reaction continues. The complex is most likely created by the coordinated transfer of an electron pair from the N-atom to Cr(VI) and oxygen from the oxidant to the N-atom. The oxidant must form a complex with the substrate in order for the nitrogen lone-pair to be used up in coordinating with an electron-deficient center, preferably a metal ion, in order to facilitate the depletion of lone-pair electron density, which is indicated by a negative q value.

3.3 Mechanism of oxidation

The oxidation of DBA by CTMABC in perchloric acid is shown in Scheme 1.

Nevertheless, the rate of oxidation is slowed down by the addition of Mn(II) (0.003 mol dm—3) in the form of MnSO4. This suggests that the Cr(IV) intermediate is involved in the Cr(VI) reagent's oxidation of DBA. Cr(IV) is reduced to Cr(III) by the Mn(II) ion. When the Mn(II) ion is absent, the generated Cr(IV) converts Cr(VI) to Cr(V), and Cr(V) quickly oxidizes DBA[22] The elimination of Cr(IV) by reaction with Mn(II) has been attributed to the decrease in the rate of Cr(VI) reduction with the addition of Mn(II)[23]

$$\mathrm{Cr(IV)} + \mathrm{Mn(II)} \rightarrow \mathrm{Cr(III)} + \mathrm{Mn(II)} \qquad (2)$$

A similar mechanism has been postulated for the oxidation of chalcones by Morpholinium Chlorochromate.Further, such a complex formation is supported by the negative entropy of activation observed. The above mechanism leads to the following rate law

$$—d[\mathrm{CTMABC}]/dt = k_1k_2k_3[\mathrm{DBA}][\mathrm{CTMABC}][H^{+}] \qquad (8)$$

3.4 Structure reactivity correlation

Some para-substituted dibenzalacetone were subjected to oxidation kinetics by CTMABC at four different temperatures (298, 303, 308, and 313 K) in a 50–50% (v/v) acetic acid–water medium in the presence of perchloric acid. The substrate effect shows that para-substituted dibenzalacetone are also first order dependent; Table 6 provides the second order rate constants at four different temperatures as well as the activation parameters. It's interesting to note that the reactivity decreases in the order p- OCH_3 > p-CH_3 > p-H > p-Cl > p-NO_2 for the substituents.

3.5 Activation parameters

Table 3 displays the activation parameters, which were determined from k_2 at 298, 303, 308, and 313 K using the Eyring relationship and the least squares approach. The response conforms to the co0mpensation law, sometimes referred to as the isokinetic connection, while not being isoenthalpic or isoentropic.

$$\Delta H^{\#} = \Delta H^{0} + b\Delta S^{\#} \quad (9)$$

The temperature at which every chemical in the series reacts at the same rate is known as the isokinetic temperature, or b. Furthermore, the free energy of activation is unaffected by the substituent's fluctuation at the isokinetic temperature.

3.6 Hammett plot

A linear free energy relationship is attempted by casting the data in Hammett equation. The value of the slope of Hammett plot is known as reaction constant (q). Reaction constant values at different temperatures are given in **Table 7.**

The sole factor influencing reactivity in an isoentropic reaction is the enthalpy of activation; the isokinetic temperature is at infinity. For an isoenthalpic series, the entropy of activation determines the reactivity, and the isokinetic temperature is zero[24,25] Using Eq. (10), the logarithms of rate constants at two distinct temperatures (T2 > T1) are plotted against one another to evaluate the isokinetic connection.

$$\log k(\text{at } T_2) = a + b \log k(\text{at } T_1) \quad (10)$$

The isokinetic connection (Figure. 15) is supported by the linear relationship in Exner plots[26,27] at 4 + log k2 (303 K) and 4 + log k2 (308 K) found in this investigation. 456 K is the predicted isokinetic temperature. All of the substituted anilines under investigation undergo oxidation via a same mechanism, according to the isokinetic relationship's operation[28].

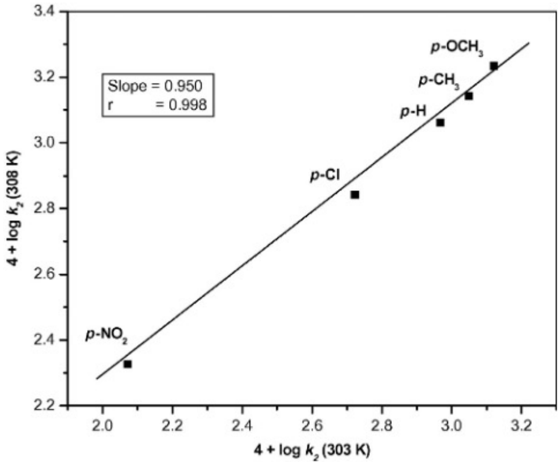


Figure 15 Exner's plot of 4 + log k_2 (308 K) versus 4 + log k_2 (303 K) for the oxidation of DBA by CTMABC.

Table 6 Activation parameters and second order rate constants for the oxidation of *para*-substituted dibenzalacetone by CTMABC in aqueous acetic acid medium.

[DBA] = 2.0 X 10^2 mol dm^{-3}; [CTMABC] = 1.0 X 10^3 mol dm^{-3}; [H$^+$] = 2.5 X 10^1mol dm^{-3}. Solvent composition = 50% AcOH – 50% H_2O (v/v)

DBA	10^2 k_2 (dm^3 mol^{-1} s^{-1})				Ea	$\Delta H^\#$	$\Delta S^\#$	$\Delta G^\#$
	298 K	303 K	308 K	313 K	(kJ mol^{-1})	(kJ mol^{-1})	(J K^{-1} mol)	(kJ mol^{-1}) (at 303 K)
H	7.15	9.28	11.54	14.05	34.83	32.30	158.36	80.28
p-OCH$_3$	10.16	13.20	17.16	21.45	38.85	36.31	143.95	79.92
p-CH$_3$	8.65	11.20	13.90	19.96	48.48	39.63	132.47	79.76
p-Cl	4.60	5.28	6.65	8.32	31.09	28.54	175.02	81.57
p-NO$_2$	1.39	1.80	2.12	2.88	26.47	33.84	166.96	84.42

Table 7 Reaction constant values at different temperatures.

<table>
<tr><td colspan="4">[DBA] = 2.0 X 10^2mol dm^{-3}; [CTMABC] = 1.0X 10^3 mol dm^{-3};
[H$^+$] = 2.5X 10 mol dm^{-3} Solvent composition = 50% AcOH – 50% H_2O (v/v).</td></tr>
<tr><td>Temperature (K)</td><td>Reaction constant, q</td><td>Correlation coefficient</td><td>Standard deviation</td></tr>
<tr><td>298</td><td>−0.8979</td><td>0.994</td><td>0.05</td></tr>
<tr><td>303</td><td>−0.8633</td><td>0.995</td><td>0.03</td></tr>
<tr><td>308</td><td>−0.8466</td><td>0.997</td><td>0.02</td></tr>
<tr><td>313</td><td>−0.8043</td><td>0.996</td><td>0.06</td></tr>
</table>

Scheme 1: Oxidation of Dibenzalacetone by CTMABC

Additionally, the Hammett plot is linear (Figure 16). Hammett asserts that electron removal from the benzene ring accelerates reactions with positive q values while it retards those with negative q values [29]. The electron-donating groups raise the rate in these oxidation processes whereas the electron-withdrawing ones lower it. The Hammett Plot provides these observations, which corroborate the negative q values.

$$H + HCrO_4^- \overset{K_1}{\rightleftharpoons} H_2CrO_4$$

$$H_2CrO_4 \overset{K_2}{\rightleftharpoons} \text{Complex (C)}$$

$$\text{Complex (C)} + \text{Dibenzalacetone} \overset{K_3}{\rightleftharpoons} \text{Chalcone epoxide} + \text{Cr(III)}$$

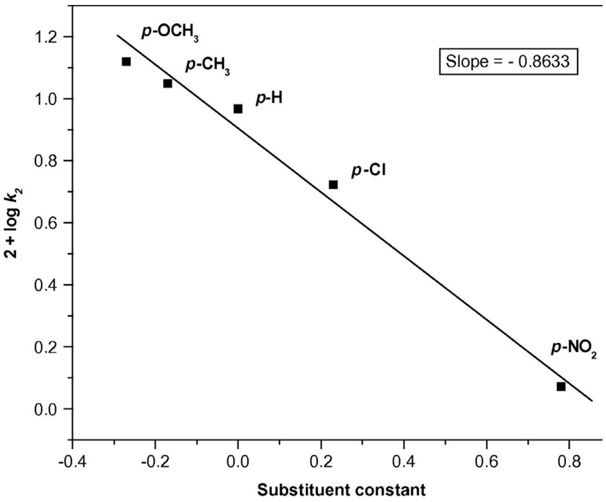
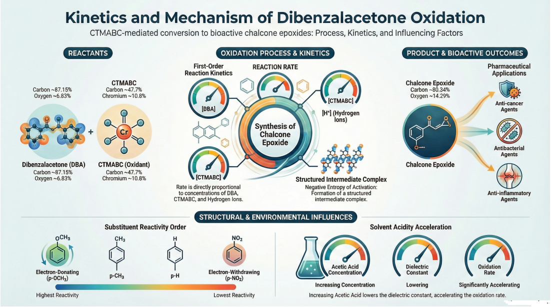


Figure 16 Hammett plot of 2 + log k_2 versus substituent constant, r at 303 K for the oxidation of DBA by CTMABC.

Graphical Abstract:



4 Conclusions

The mechanism of CTMABC's oxidation of dibenzalacetone and some para-substituted dibenzalacetone is described in depth in this work. This research work explains on the synthesis and characterizarion of oxidant like CTMABC and reactant like DBA. First order reactions occur in [DBA], [CTMABC], and [H^+]. The corresponding chalcone epoxides are produced by oxidizing para-substituted dibenzalacetones. The oxidation product chalcone epoxide was confirmed by the spectral characterization techniques.

A positively charged reactive intermediate is created during the oxidation process, as indicated by the negative q values derived from the Hammett plot. Likewise, the slow step's activation complex creation was supported by the negative value of $\Delta S\#$.

References

1. Dave, Itishri, Vinita Sharma, and Kalyan K. BANERJI. "Kinetics and mechanism of the oxidative regeneration of carbonyl compounds from oximes by quinolinium fluorochromate." *Journal of the Indian Chemical Society* 79.4 (2002): 347-350
2. Mauro M. de Oliveira , Carlos E.S. Nogueira , Francisco Wagner Q. Almeida-Neto [f], Helcio

   S. Santos, Alexandre M.R. Teixeira , Pedro de Lima-Neto, Emmanuel S. Marinho [g], Manoel O. de Moraes, Claudia Pessoa, Francisco Washington A. Barros-Nepomuceno ' Full Spectroscopic Characterization and Cytotoxicity Activity of Synthetic Dibenzalacetone Derivatives.*Journal of Molecular Structure* ,1231, 129670,5 (2021) https://doi.org/10.1016/j.molstruc.2020.129670.
3. Yuliana Purwaningsih, Erwin Indriyanti, Mighfar Syukur, Dyan Wigati, Synthesis of Dibenzalacetone using Sonochemistry and Its Antibacterial Activity Against Escherichia coli, Pathogens and Global Health 309-318,109, 7(2015) doi: 10.1179/2047773215Y.0000000030.
4. Dr. S.K. Periyasamy And Mr. R. Ponmadasamy, International Letters of Chemistry, Physics and Astronomy, Cooxidation of Dibenzalacetone with Oxalic Acid by Pyrazinium Chlorochromate, Vol. 85, pp 1-14,

doi:10.56431/p-jsue79

5. K. Rajalakshmi1 and T. Ramachandramoorthy, Oxidation of Chalcones by Morpholinium Chlorochromate withOxalic Acid as Catalyst: Kinetic and Mechanistic Study, Journal of Chemistry,Volume 2013,,1- 5 http://dx.doi.org/10.1155/2013/240102.
6. M. Vellaisamy, M. Keerthiga, Oxidative Kinetics Mechanism Of Substituted Chalcones By Imidazolium Chlorochromate, *J Adv Sci Res, 2020; 11 (4): 120-125*
7. Yousif Algamala, M. A. Embabyb and Majed H. Shtaiwi, Substituents effect on cooxidation rate of chalcones and oxalic acid using chromium (VI), Journal of Chemical and Pharmaceutical Research, 2016, 8(5):110-118.
8. T.veeraiah, s.sondu, Interactive free energy relationships in the Os (VIII) catalysed oxidation of chalcones by acid bromate, A kineic study, Indian journal of chemistry35 A,1996,1073-1078.
9. Seplappatty Kalimuthu Periyasamy* and K. Saravanakumar, Oxidation of Distyryl Ketone by Quinaldinium Chlorochromate – A Kinetic Study, *World News of Natural Sciences 13 (2017) 113-121.*
10. K. G. Sekar and S. K. Periyasamy, Oxidation of Distyryl ketone by Quinaldinium fluorochromate:A Kinetic and mechanistic study, Journal of Chemical and Pharmaceutical Research, 2012, 4(4):2153-2161.
11. P.Tamilselvi, K. Karunakaran, Kinetics and mechanism of oxidation of chalcones by 1,3-Dichloro 5,5 – dimethyl hydantoin, Asian journal of Chemistry, 27(5), 2015,1725-1728.
12. J.Anilkumar, S.sondu, Kinetics and mechanism of oxidation of chalcones by trichloroisocyanuric acid in HOAc-HClO4 medium, Indian journal of chemistry, 46 A,2007,1792-1795.
13. An. Palaniappana,R. Udhayakumarb, S. Srinivasana, and C. Raju, Kinetics and Mechanism of Oxidation of dibenzalacetone(DBA) by Isonicotinium dichromate in aqueous acetic acid medium -catalyzed by 1, 10- phenanthroline, Journal of Chemical and Pharmaceutical Research, 2012, 4(5):2385-2390.
14. Shahriar Ghammamy, Hossein Eimanieh & Mohammad Kazem Mohammady (2007): Cetyltrimethylammonium Bromochromate: A New and Efficient Oxidant for Organic Substrates, SyntheticCommunications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:4,599-605, http://dx.doi.org/10.1080/00397910601055164.

15. James M. Thompson, Infrared Spectroscopy, 1, 2018, DOI: https://doi.org/10.1201/978135120603744

16. Charlotte Vogt, Ultraviolet-Visible (UV-Vis) Spectroscopy, 18, (2023), https://link.springer.com/chapter/10.1007/978-3-031-07125-6_11

17. J.W. Akitt, B. E. Mann, NMR and Chemistry, 20 (2017), DOI: https://doi.org/10.1201/9781315274690

18. Breitmaier, E; Voelter, W, Carbon-13 NMR spectroscopy, 12, (1987), https://www.osti.gov/biblio/7169098

19. Banerji, K.K., Bishoni, M.L., Negi, S.C., Kinetics & Mechanism of Oxidation of SOIne a-Hydroxy Acids byN-Bromoacetamide in Perchloric Acid Solution1986a. Indian J Chem. 25A, 660-662.https://d1wqtxts1xzle7.cloudfront.net/98561063/298001160-libre.pdf?1676192236=&response-content-disposition=inline%3B+filename%3DKinetics_and_Mechanism_of_Oxidation_of_S.pdf&Expires=1748919291&Signature=LQoVNqgrpfxWhKtIvLrfNbahPz1eehRS2vFUpgijKujeZrqtun0Zf5KOe40aBJH4AwRhscdxPp14CcTt0k9dLzoefBX0YabwDPe

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20. Banerji, K.K., Kothari, S., Agarwal, A., Kinetics & Mechanism of Oxidation of Primary Alcohols byN -Bromo- 3,5-dinitro benzamide 1986b. Indian J. Chem. 25A, 722-724 https://nopr.niscpr.res.in/bitstream/123456789/48313/1/IJCA%2025A(8)%20722-724.pdf
21. Wiberg, W.B., 1985. Oxidation in Organic Chemisry, Part A. Academic Press, New York.
22. Karunakaran, C., Suesh, S., Identical kinetic behavior of dichromates and halochromates of heterocyclic bases: oxidations of pentan-1-ol, 2004. J. Phys. Org. Chem. 17, 88-93, https://doi.org/10.1002/poc.699

23. Khan, Z., Dar, M.Y., Babe, P.S.S., 2004. A kinetic study of the reduction of chromium(VI) by thiourea in the absence and presence of manganese(II), cerium(IV) and ethylenediaminetetra acetic acid (EDTA). Indian J. Chem. 42A, 1060–1065. https://nopr.niscpr.res.in/bitstream/123456789/18143/1/IJCA%2043A(5)%201060-1065.pdf.

24. Elango, K.P., Bhuvaseshwari, D.S., 2007a. Int. J. Chem. Kinet. 39,289.
25. Bhuvaseshwari, D.S., Elango, K.P., 2007. Solvent hydrogen bonding and structural effects on nucleophilic substitutionreactions. Part 3-Reaction of benzenesulphonyl chloride with anilines in benzene/propane-2-ol mixtures. Int. J. Chem. Kinet. 39, 657–663.
26. Exner, O., 1964. Concerning the Isokinetic Relationship. Nature, 488–490.
27. Exner, O., Streitwiser, J.R., Talt, R.W., 1973. Progress in Physical Organic Chemistry. John Wiley, New York, p. 41
28. Leffler, J.F., Grunwald, E., 1963. Rates and Equilibrium of Organic Reactions. Wiley, New York.

29. Hammett, L.P., 1940. Physical Organic Chemistry, first ed. McGraw- Hill, New York.