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Chromium(VI) Promoted Oxidative Transformations: An Integrated Review of Kinetic Models and Reaction Mechanisms

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Abstract
Chromium(VI) compounds have been used in aqueous and nonaqueous media to oxidize a variety of organic compounds over the last few decades. The main objective of the present study is to briefly summarize and explore the available literature on the oxidation kinetics study of various organic substrates by Chromic acid and Pyridinium dichromate (PDC), and to highlight their contributions to the important and exciting field of synthetic organic chemistry. The literature indicates that PDC is more stable and well-defined, allows determination of activation parameters (Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$), and is easier to use to establish the reaction mechanism than chromic acid. On the other hand, chromic acid is more complex, tends to form various Cr(VI) species depending on acidity, and can sometimes lead to over-oxidation.

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Introduction

Chromium was discovered in 1798 by French chemist Vauquelin. It is classified as a transition element in group VI-B of the periodic table, with a ground-state electronic configuration of (Ar) $3d^5$ $4s^1$. Chromium is the most common heavy metal and ranks as the twenty-first most abundant element in Earth's crust. Cr (III) is essential in human nutrition in glucose metabolism. But most of the hexavalent compounds are toxic, and cause lung cancer[1,2, 3, 4.] Chromium offers significant economic benefits across various industries, including stainless steel manufacturing, electroplating, tanning, pigment production, and the chemical sector. Recently, many researchers have been interested in oxidation processes, particularly using environmentally friendly and selective Chromium(VI) reagents. Chromium(VI) is used to oxidize organic compounds and is subsequently reduced to lower oxidation states[5]. Oxidations with Cr(VI) is a complex reaction that is influenced by the solvent, structure of the substrate, temperature, acidity of the reaction medium and other factors, hence it is difficult to study from mechanistic point of view. In recent years, development of new Cr(VI) reagents for the effective and selective oxidation of organic substrates under mild conditions has been studied because Cr(VI) is a versatile oxidant for various organic compounds[6].

The initial compound to be reported was pyridinium chlorochromate [7] (PCC) known as Corey's reagent. Their discovery has led to increased interest in the field of organic derivatives of chromium(VI) as oxidizing agents. Well-known among these derivatives are: benzyl triethyl ammonium chlorochromate [8], benzyl trimethyl ammonium dichloroiodate [9], benzotri- azole trioxide [10], biphosnium dichromate[11], bis-[benzyl trimethyl ammonium] dichromate[12], butyl triphenylphosphonium dichromate (BTPPD) [13],butyl ammonium chlorochromate and tetramethylammonium fluorochromium trioxide[14], ferric dichromate[15], imidazonium chlorochromate (ICC) and iso-quinolinium chlorochromate[16,17], imidazolinium fluoro-chromate[18],1-methyl-imidazoliniumchlorochromate(MCC),

4-(dimethylamino) pyridinium chlorochromate[19], 3,5-dimethyl pyrazole chromium(VI) complex[20], NDC and iso-nicotiniumdi chromate [21], PBC[22], 2,2'bipyridinium chlorochromate[23], 2,4-BPCC [24], PDC[25], PFC[26], napthyl pyridinium chlorochromate and pyrazinium chloromate[27], dipyridine chromium(VI)oxide complex[28], quinoliniumbromo chromate [29], quinoliniumchloro-chromate and imidazolinium dichromate [30], quinolinium dichromate[31], quinolinium fluoro-chromate[32], quinoxalinium dichromate[33], QnDC [34] and quanaldinium dichromate[35], trimethylsilylchloro chromate [36], tetraalkyl ammonium chlorochromate [37],tetrabutyl ammonium fluorochromate[38], tetrakis [pyridine] silver dichromate[39], zinc dichromate trihydrate [40], N-methylbenzyl ammonium fluorochromate (MBAFC) [41] have been reported as mild and selective oxidising agents. Mahanti and Banerji [42] reviewed the synthetic and mechanistic aspects of reactions involving complexed chromium(VI) compounds.

Experimental Discussion

Spectrophotometry has emerged as a powerful analytical tool that aligns with green chemistry principles. It allows continuous monitoring of reactions without interrupting the system, thereby reducing waste and exposure to harmful chemicals. Spectrophotometric analysis is based on the Beer-Lambert Law, which relates absorbance (A) to concentration (c)

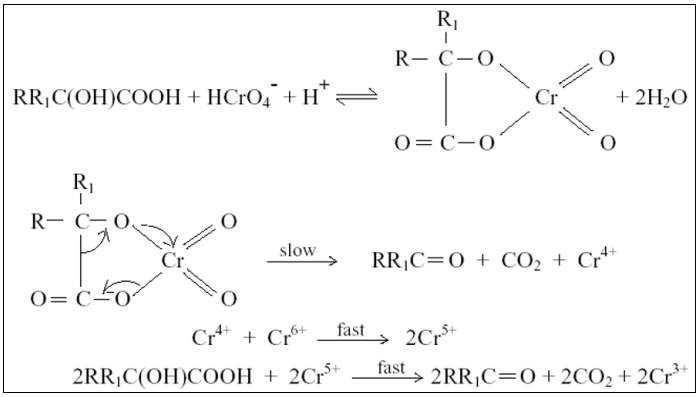
$A = \varepsilon \cdot l \cdot c$ Where: ε = molar absorptivity, l = path length, c = concentration

By measuring absorbance at different time intervals, concentration changes can be tracked, enabling the determination of reaction order and rate constants. Recent advances in green analytical chemistry have emphasized the development of environmentally friendly, efficient, and reliable methods for pharmaceutical analysis. Here is the literature review of the kinetic study of oxidation reactions by chromic acid and PDC (Pyridinium chlorochromate).

Chromic Acid as an Oxidant

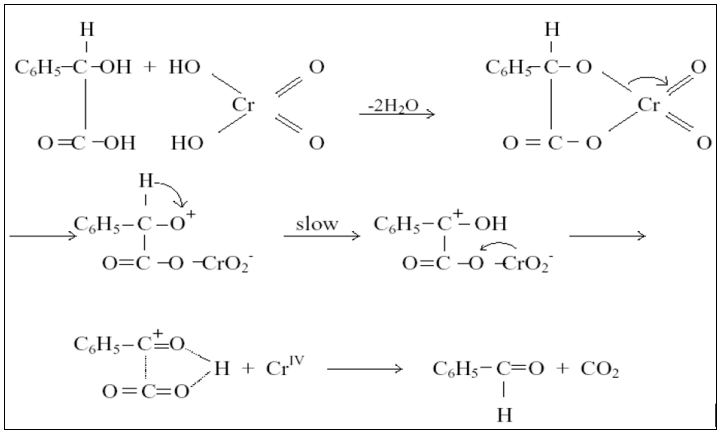
Chromic acid is a highly versatile oxidizing agent that reacts with a wide range of substrates. It has been widely used for oxidizing both inorganic [43, 44] and organic compounds [35-48]. In aqueous solutions in the absence of other ions [49], chromic acid exists as $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. At concentrations above 0.05 M, the dichromate ion and its protonated forms are the main species. In very dilute solutions, Chromium(VI) is primarily monomeric. In basic solutions (pH > 7), the acid chromate ion, $HCrO_4^-$, loses a proton, and it acquires a second proton within the pH range of 1 to 3.

Oxidation kinetics [50] of several α-hydroxy acids, including mandelic, lactic, benzilic, and benzyl phenylglyoxylic acids, follow a first-order reaction with respect to both the oxidant and each substrate. The reaction was acid-catalyzed with a first-order dependence on (H^+). Both $HCrO_4^-$ and $Cr_2O_7^{2-}$ appeared to participate, aligning with oxidation and product analysis results. A proposed reaction pathway involves forming a cyclic chromate ester (Scheme 1), with the rate-limiting step being oxidative decarboxylation. The oxidation process involved a two-electron transfer.



Scheme 1: Proposed Reaction mechanism of α-hydroxy acids with Chromic acid.

Ramanathan and Varadarajan [51] investigated the oxidation kinetics of benzoin with chromic acid, finding that the rate depended linearly on the concentrations of both benzoin and Cr (VI). A new mechanism [52] is introduced for the oxidative decarboxylation of mandelic acid, supported by deuterium-labeling studies and solvent isotope effects. (Scheme-2)



Scheme 2: Proposed Reaction Mechanism of Benzoin with Chromic Acid

The described mechanism was suggested for decarboxylation, starting with the formation of a cyclic anhydride. This intermediate then decomposes, allowing a hydride ion to transfer from the α-carbon to the neighboring electron-deficient oxygen. This pathway is plausible because the positive charge on the α-carbon can be stabilized by the electron cloud of the benzene ring.

Islam *et al*. [53] examined the oxidation kinetics of d,l-mandelic acid using chromic acid, both with and without 1,10-phenanthroline (Phen), in an aqueous micellar medium where [d,l-mandelic acid] significantly exceeds [Phen]T, which in turn exceeded [Cr(VI)]T at various temperatures. By analyzing how temperature affects the rate constant (k), they determined the activation parameters $\Delta H^{\neq}$ (enthalpy of activation) and $\Delta S^{\neq}$ (entropy of activation) using the Eyring equation, where a high $\Delta H^{\neq}$ suggested the phen-catalyzed pathway was preferred mainly due to a highly negative $\Delta S^{\neq}$. The negative $\Delta S^{\neq}$ and the composite rate constant supported a cyclic transition state hypothesis. Both catalytic and non-catalytic pathways exhibited first-order kinetics with respect to $[H^+]$, [d,l-mandelic acid]T, and [Cr(VI)]T, with the phen-catalyzed pathway also being first-order in [Phen]T.

The influence of cationic, anionic, and neutral surfactants on the Cu (II)- facilitated oxidation of L-phenylalanine using chromic acid under kinetic conditions was examined by Srivastava *et al*. [54] The oxidation rate was determined by measuring the decrease in absorbance at 350 nm, which is an indicator of Cr(VI) concentration. The reaction progress was assessed using the pseudo-first-order condition as a gauge of $[H^+]$, [Cr(VI)], ionic strength, [Cu(II)], [Surfactant], and temperature. Phenylalanine and Cr(VI) interacted in a 3:2 stoichiometric ratio.

PDC as an Oxidant

PDC was first isolated by Sisler and colleagues [53] from the reaction between chromium trioxide and pyridine. Challenges associated with handling Collins reagent and issues caused by the acidic nature of Corey's reagent were addressed using Pyridinium dichromate (PDC), a mild and selective oxidant. PDC $[(C_5H_5NH)_2]$ $[Cr_2O_7]$ is a stable, bright orange solid (M.P. 144–146 °C) and is prepared by dissolving CrO_3 in a minimum amount of water, adding pyridine, and collecting the precipitated product [54]. The composition and structure of the product were confirmed by elemental analysis and infrared spectroscopy, which showed bands at 930, 875, 765, and 730 cm^{-1}.

In dichloromethane, PDC effectively oxidizes primary and secondary alcohols. When dissolved in DMF, it can oxidize allylic alcohols to the corresponding α, β-unsaturated aldehydes.

PDC dissolves in acetonitrile; the solution is unstable. Most of the experiments have been carried out with PDC solutions in DMF or in suspensions in methylene chloride. It liberates iodine with an aqueous acidic solution as follows:

$$(PYH)_2\ Cr_2O_7 + 6KI + 3H_2SO_4 \rightarrow 2PY + H_2O + Cr_2O_3 + 3K_2SO_4 + 3I_2$$

Allylic alcohols were oxidized more rapidly than aliphatic alcohols by PDC. For instance, cyclohexanol oxidized ten times faster than cyclohexenol in dichloromethane at 25ºC [19]. Meanwhile, primary aliphatic alcohols also underwent oxidation, but only under very mild conditions [55]. This process takes place under approximately neutral pH.

Cyclohexenol was oxidized to cyclohexanone with an 86% yield using PDC in DMF at 0ºC [19]. Likewise, geraniol was converted to geranial with a 92% yield. It is important to note that treating non-conjugated primary alcohols with PDC in DMF at room temperature often yields carboxylic acids rather than aldehydes. Oxidation [56] of certain aliphatic primary and secondary alcohols, as well as cyclohexanol and benzyl alcohol, using PDC as the oxidant was investigated. The reactions took place in a 30% dioxane-water (v/v) mixture. The process was first-order with respect to both [PDC] and [alcohol]. Additionally, the rate constant increased with increasing $[H^+]$ concentration.

Kabilan *et al*. [57] examined the reaction of benzyl alcohol with twenty–five mono-substituted derivatives at ortho, meta, and para positions. The kinetics were monitored spectrophotometrically in dry acetonitrile acidified with trichloroacetic acid (TCA), using pyridinium dichromate (PDC) as the oxidant under pseudo-first-order conditions relative to PDC. Benzaldehyde was identified as the sole oxidation product, and no reaction occurred in the absence of TCA. The study found that Hammett reaction constants decreased in magnitude as temperature increased.

A kinetic [58] study of the oxidation of certain primary and secondary alcohols using PDC was conducted. Oxidation was facilitated by p-TsOH in acetonitrile. The reaction showed a first-order dependence on PDC and followed Michaelis-Menten kinetics with respect to the alcohol. TsOH increased the reaction rate, whereas pyridine substantially slowed it down due to a parallel competitive reaction with TsOH. They also observed water formation even under anhydrous conditions.

Oxidation kinetics of aryl methyl sulphides (CH_3SAr) with PDC in an aqueous acetic acid medium, yielding in sulphoxides studied by Mangalam *et al* [59]. They explained the substituent effect through an electrophilic attack by PDC oxygen on the sulphide, which creates a polar transition state. The addition of Mn (II) significantly slowed the reaction, indicating the involvement of transient species. Furthermore, electron-donating substituents speed up the reaction, while electron-withdrawing groups slowed it down.

Many authors [60] investigated the oxidation of oxime by PDC in 60% acetic acid-water mixtures (v/v). They observed that the reaction was first order with respect to [oxidant], second order with respect to [substrate], and zero order with respect to hydrogen ion concentration. Meanwhile, Girija and Kabilan [61] examined the oxidation of cycloalkanol by PDC in MeCN medium with trichloroacetic acid present, finding that the reaction was first order in each of [oxidant], [substrate], and [TCA]. An increase in the dielectric constant of the medium raised the rate, while the addition of perchlorate ion had no significant impact.

Oxidation of organic sulfides [62] using PDC in acetonitrile was studied by Meenakshisundaram *et al*. [62]. They observed that the reaction rate depends linearly on both PDC and sulphide, with a quadratic dependence on TsOH. For aryl-methyl sulphides, the reaction order concerning TsOH ranges from 1 to 2, and a Michaelis-Menten kinetic pattern appears with respect to sulphide concentration. Moreover, the presence of acetonitrile slowed the reaction, indicating a one-electron oxidation mechanism that generates free radicals.

Dangarh *et al*. [63] examined the oxidation kinetics of lactic acid by PDC in perchloric acid medium. The active oxidizing species identified was protonated PDC. They investigated how the concentrations of PDC, $HClO_4$, Mn (II), Ce(III), and ionic strength influenced the reaction. The reaction order with

respect to lactic acid was one. The presence of Mn (II) and Ce (III) ions slowed the oxidation rate. A cyclic complex formation that undergoes C–C bond fission was proposed.

The oxidation of aliphatic alcohols by PDC in a non-aqueous medium at 303 K produces the corresponding aldehydes [64]. In this process, Cr(VI) acts as a two-electron oxidizing agent. The reaction is first order with respect to each of the oxidant, [TsOH], and [Alcohol]. A decrease in the dielectric constant of the medium accelerates the reaction rate

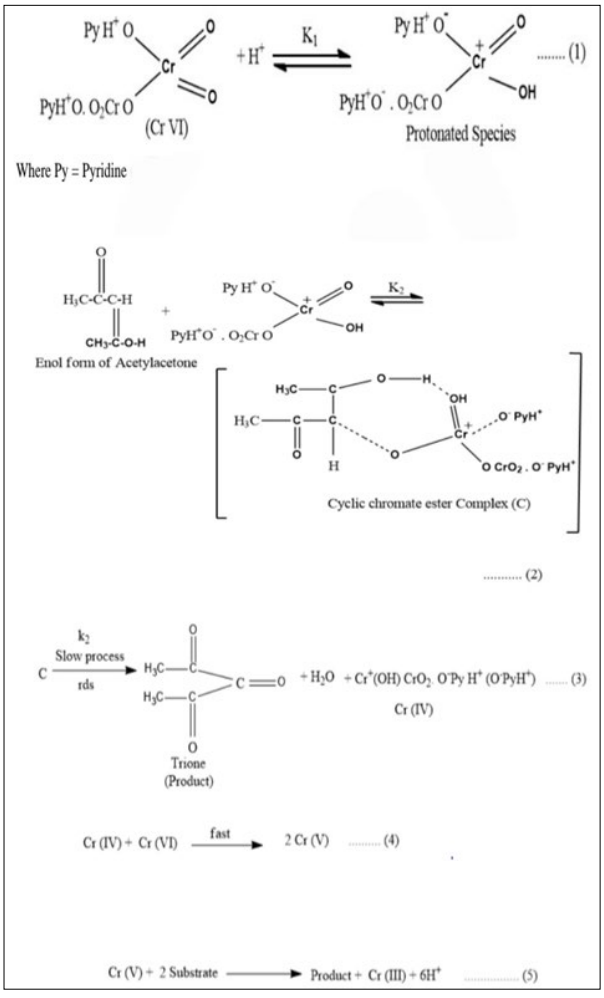
Kinetic behavior of both simple and substituted anils under various conditions, including different solvents, oxidants, electrolytes, catalysts, catalyst mixtures, and temperatures were studied by Krishnaswamy *et al*. [65]. Oxidation of S-phenylmercaptoacetic acid [66] and phenoxyacetic acid using PDC was studied. Additionally, Gurumurthy *et al*. [67] conducted a comparative analysis on the oxidation kinetics of some secondary alcohols using 1-chlorobenzotriazole and pyridinium dichromate.

Ahmed *et al*. [68] investigated the kinetics and mechanism of oxidizing some α-hydroxy acids using pyridinium dichromate (PDC) in a 50% acetic acid-50% water (v/v) mixture at 303K, employing spectrophotometry. Under pseudo-first-order conditions, the reaction exhibited first-order kinetics relative to hydroxy acid, [H^+], and [PDC]. The reaction rate increased with higher acetic acid percentage, and the plot of log K_{obs} versus 1/D was straight with a positive slope, suggesting an ion-dipole mechanism.

The oxidation of thioglycolic, thiolactic, and thiomalic acids by PDC in DMSO (dimethyl sulfoxide) was investigated by Sharma *et al*. [69]. The reactions followed first-order kinetics with respect to PDC and displayed Michaelis–Menten type behavior with respect to substrate concentration. Hydrogen ions catalyzed the reaction, and solvent effects were interpreted using Kamlet–Taft and Swain solvent parameters. The Researchers suggested the formation of a thioester intermediate prior to the rate-determining decomposition step.

Oxidation of active methylene compounds like acetylacetone and benzoylacetone using pyridinium dichromate (PDC) in aqueous formic acid with mineral acid was examined by Sahu and Manikpuri [70]. Acetylacetone converted into pentane-2,3,4-trione, and benzoylacetone converted into 1-phenylbutane-1,2,3-trione. The reaction rate was proportional to PDC and hydrogen ion concentrations, showing almost first to zero-order dependence on substrate. The process did not trigger acrylonitrile polymerization, indicating no free radicals. Data supported a mechanism where an intermediate complex form through a symmetrical transition state in the rate-determining step, then decomposes to produce the oxidation products. Oxidation kinetics of ethyl acetoacetate (EAA), an active methylene compound, in acetic acid, which yields α-β-diketobutyric acid, was examined [70]. They observed Michaelis-Menten kinetics for the substrate ester, with the reaction rate directly proportional to the oxidant PDC. The oxidation process accelerated with higher proton concentration. Solvent polarity indicated that the reaction involved ion-ion dipole interactions. Based on the measured activation parameters, a mechanism is proposed in which the rate-determining step is the decomposition of a complex through a cyclic transition state. The proposed mechanism for this reaction is as follows:

Scheme 3.



Scheme 3: Proposed Reaction mechanism of Ethylacetoacetonate with PDC

Conclusion

Oxidation of various organic substrates with Chromic Acid and PDC, studied by different investigators, is reported above. Transition-metal complexes have been of great interest over the last few years, largely due to their diverse biological applications and potential for the design of new therapeutic agents. Using PDC as an oxidant offers several benefits, including its chemical stability, ease of preparation, and typical first-order kinetics with respect to the oxidant. It reduces complications due to chromium speciation and enables reliable determination of activation parameters (Ea, $\Delta H^{\neq}$, $\Delta S^{\neq}$). PDC is effective for oxidizing alcohols, aldehydes, ketones, amino acids, and various organic substrates. Mechanistic models involving chromate ester formation are often clearer with PDC, unlike chromic acid, which exists in equilibrium among several Cr(VI) species such as H_2CrO_4, $HCrO_4^-$, $HCrO_{4-}$, and $Cr_2O_7^{2-}$, with the distribution highly dependent on pH and chromium concentration. As a result, kinetic orders can vary with acidity, multiple reactive species may be involved, and the mechanistic interpretation becomes more difficult. Therefore, pyridiniumdichromate (PDC) is generally preferred over chromic acid (H_2CrO_4) for most laboratory kinetic studies.

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