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Kinetics and Mechanistic Signatures in the Oxidation of α-Hydroxy Acids by PCC, PDC, QDC and TBAD: A Comprehensive Comparative Study

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Abstract

The oxidation of α-hydroxy acids by chromium(VI) provides a valuable system for differentiating weakly associated chromate-ester pathways from strongly organized cyclic inner-sphere mechanisms. A systematic kinetic comparison of glycolic, lactic, and mandelic acids with pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), quinolinium dichromate (QDC), and tetrabutylammonium dichromate (TBAD) was performed under controlled acidic conditions. All systems obey pseudo–first-order kinetics with respect to chromium(VI). PCC and PDC exhibit linear substrate dependence, whereas QDC and TBAD display saturation kinetics consistent with reversible substrate–oxidant complex formation. Acid-dependence studies reveal near-first-order proton involvement for PCC (slope ≈ 1.0) and saturation behavior for QDC and TBAD. Activation entropies become progressively more negative across the oxidant series (PCC: −28 J mol^{-1} K^{-1}; TBAD: −89 J mol^{-1} K^{-1}), indicating increasing transition-state organization. The combined kinetic and thermodynamic parameters establish a consistent mechanistic ordering across the oxidant series governed by counterion lipophilicity and solvation effects.

Introduction

Chromium(VI)-mediated oxidation of organic functional groups represents one of the most extensively studied areas of mechanistic inorganic and organic chemistry. Over the decades chromium(VI) compounds such as chromates and dichromates and a variety of organo-chromium(VI) salts have been used as potent oxidants that change alcohols, α-position acids, allylic substrates, activated methylenes, and other species bearing oxygen with great selectivity. The unique property of Cr(VI) as a multi-electron reducing agent that at the same time catalyzes oxidative reactions in organic substrates places these reagents at the interface between inorganic redox chemistry and organic oxidation pathways [1]. Chromium(VI) oxidations despite their extremely long history still lie central to the discussion of mechanisms due to their wide range of possible pathways and high sensitivity to solvent and protonation effects, as well as their ability to populate either loose outer-sphere or tight inner-sphere intermediates. Alpha-position carboxylic acids represent an especially instructive group of substrates oxidized by chromium(VI). These substrates also have a hydroxyl group that can be coordinated to chromium both a carboxyl group that can undergo hydrogen bonding, acetylation or chelation. Due to the potential of bidentate coordination, there is the potential of cyclic chromate ester formation a structural intermediate to inner-sphere electron transfer and oxidative decarboxylation. Meanwhile, the α-position is electronically active: electron density is regulated with substituents on the α-carbon and has a subsequent effect on the stability of the transition state. Consequently, the mechanistic information derived in α-position acid oxidations usually goes beyond both actually studied substrates and gives more extensive information regarding the transition-state structure, ligand involvement, and solvent control in Cr(VI) chemistry [2]. Early mechanistic proposals often invoked loosely associated pathways with minimal pre-equilibrium complex formation. However, modern understanding recognizes that even PCC-mediated oxidations proceed through chromate ester intermediates, though with limited stabilization relative to more lipophilic oxidants. The oxidation of simple alcohols served as an additional source of reinforcement to such interpretations and in that case often only through participation of hydrogen abstraction of the substrate [3]. Nonetheless with a multiplicity of structurally different Cr(VI) reagents appearing around, e.g., pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), and then more lipophilic reagents, like quinolinium dichromate (QDC) and tetrabutylammonium dichromate (TBAD) it became increasingly obvious that Cr(VI) does not act uniformly. Different chromium(VI) oxidants exhibit distinct mechanistic signatures governed by counterion structure, solvation, and medium polarity. Pyridinium chlorochromate (PCC) typically operates through weakly organized chromate-ester pathways, whereas more lipophilic oxidants such as quinolinium dichromate (QDC) and tetrabutylammonium dichromate (TBAD) facilitate stronger substrate association and cyclic transition-state formation, counter-ion structure and medium polarity. As an example, PCC is a low-potency acidic reagent of Cr(VI) commonly employed in organic synthesis in the transformation of primary alcohols to aldehydes. It is very medium-dependent and tends to be explained by a loose association model of limited prior coordination of substrate and chromium. Conversely, PDC exhibits greater oxidative potential and is reported to make more organized reactions with substrates in polar protic solvents [4,5]. The quinolinium cation, larger in size, slightly less hydrophilic, higher lipophilicity, and thus QDC can move closer to the substrates, and create pre-equilibrium assemblies that favor cyclic intermediates. The extremely hydrophobic tetrabutylammonium counter-ion of TBAD takes these properties to their mechanistic limit: its low solvation shell and high ability to solubilize the organic phase values it as a prime candidate of inner-sphere, tightly interacting oxidation pathways [6]. This mechanical diversity is an asset and a problem. It also on the one hand allows the selective oxidation of structurally diverse substrates, and on the other, makes it difficult to assign a mechanism except by a systematic comparative study under controlled conditions. Although the importance of these oxidants is undoubted in both synthetic and mechanistic chemistry, it has surprisingly little comparative systematic research in which a common set of substrates is examined under a common set of experimental conditions. The sources are fairly fragmented between single study articles, which concentrate on single oxidants and may have narrow classes of substrates and therefore may be hard to generate broad mechanistic hierarchies. To fill this gap, the current paper will carry out a multi-faceted integrated kinetic and mechanistic study of oxidation of prototypic α-position acids, viz., glycolic acid, lactic acid, and mandelic acid by PCC, PDC, QDC, and TBAD in controlled solvent-acidic conditions. It is a selective arrangement of substrate oxidant pairs. The introduction of a moderately electron-donating substituent and further stereoelectronic complexity in lactic acid, and aromatic character and substituent-dependent electronic modulation in the α-carbon of mandelic acid. The ability to follow this relationship between simple and complex substrates enables the mechanistic propensity of oxidants to be seen within a range of coordination and electronic surroundings. We use four major kinetic probes to obtain mechanistic signatures of these systems namely (i) pseudo-first-order studies, (ii) substrate-dependence studies, (iii) acid-dependence studies and (iv) temperature-dependence studies with complete extraction of the activation parameters. The complementary mechanistic understanding is attained with each of these experimental dimensions. Pseudo-first-order rate constants give the background rate constants that are required to compare the mechanisms [7]. Substrate-dependence experiments show that either a simple bimolecular process is taking place or that saturation-type dependence is indicative of the existence of pre-equilibrium complexes of substrate and chromium [8]. In acid-dependence studies, the difference between oxidants where electrophilicity is sensitive to protonation and oxidants with less electrophilicity dependent on protonation is made. Arrhenius and Eyring studies exemplify temperature-dependence studies, which give activation entropies that serve as effective diagnostics to transition-state organization. The strong negative entropies of activation in chromium(VI)) oxidations are generally considered to be characteristic of inner-sphere, cyclic transition states, and weakly negative or even positive entropies characterized outer-sphere involvement or relaxed association [9,10,11]. Novelty of this work does not merely consist in the range of parameters of kinetics studied but comparative framework as well. By examining the mechanistic shifts of four oxidants of progressively increasing lipophilicity and decreasing solvation under the same conditions of reaction, a direct mapping of mechanistic shifts is possible across the oxidant series. More to the point, a combination of all four kinetic probes along with product and stoichiometric analysis gives one an integrated, internally consistent mechanistic image. This has not been done in many instances with various Cr(VI) oxidants on a representative substrate platform and so this work is of interest as a reference map to the wider understanding of policy of the Cr(VI) oxidation chemistry. The other reason why this comparative study is of interest is the increased significance of the choice of minimal-waste oxidants and the configuration of reactions whose mechanistic insights are easier to understand predictably. Although chromium(VI) reagents still pose challenges to the environment, as they are toxic and persistent, the exceptional mechanistic complexity of the reagents still guides the development of more sustainable oxidation systems, such as chromium mimetics or Cr VI -free oxidation catalysis [12,13]. Mechanistic clearness to chromium systems thus has conceptual worth that goes beyond their current synthetic uses. PCC is at the other extreme of organization end, exhibiting simple pseudo-first-order kinetics, linear dependence on substrates, near unitary acid order, and weakly negative activation entropies. PDC, however, behaves in an intermediate manner: A modest curvature in substrate dependence, and slightly negative values of activation entropies, indicate partial pre-association and moderate transition-state organization. QDC exhibits high levels of mechanistic evidence of inner-sphere coordination such as strong substrate saturation, acid saturation and highly negative activation entropies indicative of transition states cycles or structural constraints [13,14,15]. These properties are further exaggerated in TBAD, whose substrate-coupling being exceptionally strong, its entropy loss is large and it is highly sensitive to electronic structure (as observed in our companion study of Taft-correlation). TBAD is thus identified as a new benchmark oxidant of mechanistic inner-sphere reactivity by Cr(VI).

Experimental Section

1. Materials and Reagents

All alpha-position acids and the chromium(vi) oxidants used in this work were acquired commercially as pure form and they were not further purified unless stated otherwise. They were also obtained at Sigma-Aldrich in the form of glycolic acid (99%), lactic acid (88% aqueous solution) and mandelic acid (99% replaced by other acids). To ensure that the appropriate weighing is done, dried crystalline products were dried in a desiccator in the presence of phosphorus pentoxide and the process lasted several hours. Prior to the preparation of the stock solutions, the lactic acids solutions were titrated and made standard using standardized sodium hydroxide. From Lancaster, Avra and Spectrochem, pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), quinolinium dichromate (QDC) and tetrabutylammonium dichromate (TBAD) were brought as the form of analytical grade. Meanwhile, where necessary, PCC and PDC were prepared freshly with standard reported protocols with chromium trioxide and the corresponding pyridinium salts [16-19]. The sodium dichromate quinolinium chloride metathesis reaction in aqueous solution produced QDC which needed to be filtered and dried in the vacuum. The metathesis reaction of tetrabutylammonium bromide and sodium dichromate as a purification method was carried out and the product recrystallized using acetone, in order to eliminate inorganic salts. All solids of Cr(VI) were stored in amber glass bottles under the conditions of high safety and high ventilation. The solvents were of analysis grade. Experiments involving PCC, PDC and QDC have been conducted in acetic acid-water (30% v/v), and TBAD in DMSO-water (30% v/v) because these two solvents are lipophilic, and because they are more polar solvents respectively. Primary standard sodium carbonate was used to standardize perchloric acid solutions that had been used to keep acidity. All through the research, distilled-deionized water was used.

2. Solutions Preparation and Standardization.

The right mix of solvents (30 percent acetic acid or 30 percent DMSO-water) was used to dissolve the right amount of solid oxidant, which was then weighed and added to the correct volume of solvents. To identify the concentration of these stock solutions, the most reliable and most acceptable method of quantification of Cr(VI), the iodometric titration of these stock solutions was performed. Here, a solution of the oxidant inventory was transferred into a solution which contained more potassium iodide in a mildly acidic manner in which an iodine was formed which had the same stoichiometric ratios as the Cr(VI) in solution. The liberated iodine was in turn titrated against the standardised sodium thiosulfate with the help of the starch as an indicator. The Cr(VI) concentration was determined based on the quantity of thiosulfate and its reproducibility of +-0.5 was found to be greater or less. In the case of the substrate stocks, the accurate weight of glycolic acid, mandelic acid or standardized lactic acid was dissolved in the working solvent system. Normally the concentration of the substrates was 0.5-1.0 mol dm^{-3} as such that it was easy to establish pseudo-first-order. The substrate solutions had been stored in amber-capped tightly capped flasks to avoid contaminations and hydrolysis. The stock solutions of perchloric acid (1.0 mol dm^{-3}) were diluted and their dilution was made volumetrically to obtain the desired perchloric acid concentration in the kinetic experiments. All the acidic solutions were allowed to stabilize at ambient laboratory temperature and then used.

3. Instrumentation

Kinetic determinations were run on a Jasco V-730 UV Visible, spectrophotometer that had a temperature maintained in a cell holder which was connected to high-precision circulating water bath with the ability to maintain the temperature within a range of -0.1 degree C. All spectrophotometer measurements were performed in quartz cuvettes with a path length of 1 cm to ensure clarity over the spectral range being analyzed optically. The absorbance variation was monitored at the suitable values of λmax of each Cr (VI) specimen. PCC, PDC, QDC and TBAD showed fine absorption at the wavelengths of 360-460nm with the fine absorption measurements applied at the peaks of each oxidants spectral profile contributing to the maximal sensitivity. The spectrophotometer could record the data in fixed time intervals of 0.5-10 seconds respectively on the speed of the reaction using the kinetic acquisition mode. Every experiment involving temperature involved the same spectrophotometer–bath system to ensure consistency in all the results of that experiment.

4. General Kinetic Procedure

Kinetic experiments were conducted under pseudo first-order conditions with the excess of the substrate at least 10-20-fold over the concentration of the oxidant concentration. This made the concentration of substrate held constant in the entire duration of the reaction hence making the decay of Cr(VI) concentration first order with respect to the oxidant [20-21]. The overall volume of the reaction in every experiment was 3.00 mL. Oxidant and substrate solutions were heated in thermostatted bath at least 15 minutes in separate solutions. Reaction was initiated by adding rapidly the pre-thermostatted solution of the substrate to the oxidant in the cuvette or a small mixing vessel based on the rate. Mixing was carried out in all experiments with the consideration of the minimization of dead time. The cuvette was put in the spectrophotometer right after mixing and the reading of the absorbance-time was triggered. The absorbance decay followed exponential behavior. The first-order rate constant, k(obs) was obtained by slope of the linear portion of the plot. At least three kinetic runs were done on each experimental point, with the mean value of, k(obs) being used in mechanistic interpretations. Usually standard deviations were less than 2.5%.

5. Studies Depending on Substrate

To establish the reaction order concerning substrate experimental work was carried out at a fixed concentration of oxidants but variable concentration of substrates in an appropriate range. In the case of glycolic acid, lactic acid and mandelic acid, concentration values had been manipulated between 0.02 to 0.15 mol dm -1/3 based on solubility and reaction speed. The order of the substrates was determined using plots of, k(obs) versus [S] plots. Linear dependence meant that there was a first-order dependence on substrate and a bimolecular dependence. Curved plots which showed saturation at higher concentrations of substrates indicated that a pre-equilibrium complex between substrate and oxidant had formed. It was a crucial distinction that allowed the distinction to be made between outer-sphere mechanisms (which showed linear dependence on substrates) and inner-sphere mechanisms (which exhibited saturation behaviour). These trends were always dissimilar between oxidants. Both PCC and PDC produced linear or nearly linear rates with all substrates, indicating little action of substrate coordination in the rate limiting step. QDC and TBAD, by contrast, displayed pronounced curvature in the case of mandelic acid and, to a lesser extent, lactic acid, indicating significant pre-association consistent with mechanistic expectations of inner-sphere pathways[22,23,24].

6. Acid-Dependence Studies

The influence of proton concentration on reaction rate was examined by varying perchloric acid concentration over the range 0.2–1.0 mol dm^{-3} while holding substrate, oxidant, and solvent composition constant. Proton concentration is known to modulate the electrophilicity of chromium(VI) and affect substrate protonation. Therefore, understanding acid dependence is crucial for accurate mechanistic classification.

7. Temperature-Dependence and Activation Parameter Determination

For selected systems, pseudo–first-order rate constants were determined at four or five temperatures within the range 25–45 °C. Arrhenius plots (ln k vs 1/T) and Eyring plots (ln k/T vs 1/T) were constructed to determine the activation energy (E_a), enthalpy of activation (ΔH‡), entropy of activation (ΔS‡), and free energy of activation (ΔG‡).

PCC-mediated oxidations showed moderately negative ΔS‡values (–20 to –30 J mol^{-1} K^{-1}), indicative of mild ordering in the transition state. PDC exhibited intermediate values (–40 to –60 J mol^{-1} K^{-1}), whereas QDC and TBAD produced highly negative ΔS‡values (–60 to –90 J mol^{-1} K^{-1}), are strongly consistent with highly ordered transition states characteristic of cyclic inner-sphere pathways.

Activation energies were consistent with these trends, with higher E_a values corresponding to more structured transition states.

Results and Discussion

1. Kinetic Order and General Rate Behaviour

The oxidation of glycolic, lactic, and mandelic acids by pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), quinolinium dichromate (QDC), and tetrabutylammonium dichromate (TBAD) was investigated under pseudo–first-order conditions with substrate in excess. All systems exhibited clean exponential decay of chromium(VI) absorbance. Linear plots of ln(A_t) versus time were obtained over at least 85% of reaction progress, with correlation coefficients (R^2) greater than 0.995, confirming first-order dependence on chromium(VI). The observed first-order rate constants, k(obs), obtained at 30.0 °C under equimolar kinetic conditions, are summarized in Table 1.

Table 1: Typical k(obs) values at 30.0 °C for equimolar kinetic conditions

Substrate	PCC ($\times10^{-4}$ s^{-1})	PDC ($\times10^{-4}$ s^{-1})	QDC ($\times10^{-4}$ s^{-1})	TBAD ($\times10^{-4}$ s^{-1})
Glycolic acid	1.12	1.96	3.84	6.72
Lactic acid	0.89	1.54	3.21	5.95
Mandelic acid	0.42	1.12	4.78	8.63

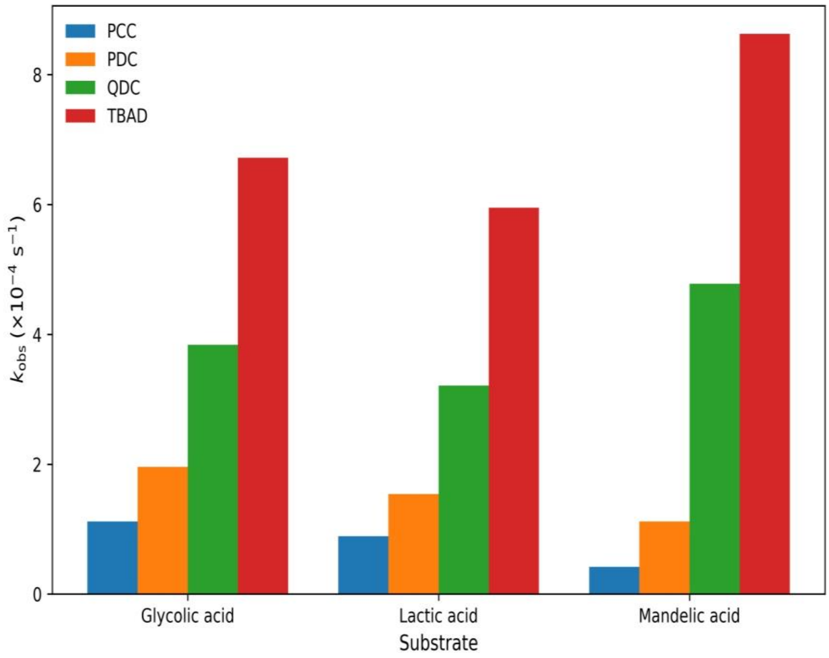

Fig 1: Comparison of observed pseudo–first-order rate constants, k(obs), for the oxidation of glycolic acid, lactic acid, and mandelic acid by pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), quinolinium dichromate (QDC), and tetrabutylammonium dichromate (TBAD) at 30.0 °C under equimolar kinetic conditions.

The comparative reactivity of the four chromium(VI) oxidants under identical conditions is illustrated in Figure 1, which shows a systematic increase in k(obs) from PCC to TBAD for all three α-hydroxy acid substrates. There are a number of immediately mechanistically significant tendencies arising out of these data. To begin with, the reactivity of all substrates increases in a systematic way of PCC < PDC < QDC < TBAD. The ordering of this reaction is based on a gradual loss of solvation and gain in electrophilic accessibility of the chromium (VI) center upon increase of the bulk of the counterion and its lipophilicity. The behavior is also reported in the case of Cr(VI) oxidants in a non- aqueous media where ion pairing and solvent separation are the determinant factors in the reaction rate. While mandelic acid is the least reactive substrate toward PCC, it becomes the most reactive substrate toward QDC and TBAD, indicating a mechanistic shift toward pathways that favor aromatic stabilization and cyclic ester formation. Lastly, TBAD provides the largest rate constants whether investigating substrates of choice. The reasoning behind this behavior is that this molecule has a very low solvation barrier and a high affinity to generate tightly bound substrateoxidant complexes and thus enables a fast inner-sphere electron transfer. These initial observations form a background structure to the finer analysis of the mechanism to be used in the following sections.

2. Substrate Dependence and Evidence for Pre-Equilibrium Complex Formation

Linear Substrate Dependence: PCC and PDC Systems

The dependence of k(obs) on substrate concentration was investigated by varying the concentration of α-hydroxy acids in the range 0.02–0.12 M while maintaining constant oxidant concentration (5×10^{-4} M). Representative data for the oxidation of lactic acid by PCC at 30.0 °C are presented in Table 2.

Table 2: k(obs) vs [Lactic Acid] for PCC

[Lactic acid] (M)	k(obs) ($\times 10^{-4}$ s^{-1})
0.02	0.28
0.04	0.57
0.06	0.85
0.08	1.12
0.10	1.41

A strictly linear relationship between k(obs) and substrate concentration was obtained, yielding the rate law:

k(obs)= 0.0141 [S] (r = 0.999)

Linear regression analysis was performed using least-squares fitting, with standard errors in slope values below 5%. Correlation coefficients (R^2) exceeded 0.995 in all systems.

The absence of curvature in the k(obs) vs [S] plot indicates that chromate ester formation, if present, does not accumulate to kinetically significant levels prior to the rate-determining step. The reaction therefore proceeds through a weakly associated chromate-ester-mediated pathway rather than through strongly organized pre-equilibrium complex formation. The same linear behavior was exhibited in the case of the PDC systems, however with steeper slopes, which is expected given the fact the PDC has a bit more organizational capacity compared to the PCC.

Although PDC exhibits largely linear dependence on substrate concentration, slight upward deviations from strict linearity were observed at higher substrate concentrations (data not shown), suggesting weak pre-association. This behavior positions PDC mechanistically between PCC and QDC, reflecting moderate chromate ester stabilization but without strong saturation kinetics.

Saturation Kinetics: QDC and TBAD Systems

In sharp contrast to PCC and PDC, QDC and TBAD exhibit pronounced saturation behavior with respect to substrate concentration. Representative data for the oxidation of mandelic acid by QDC at 30.0 °C are shown in Table 3.

Table 3: QDC – Mandelic Acid (Saturation Behaviour)

[Mandelic acid] (M)	k(obs) ($\times 10^{-4}$ s^{-1})
0.02	1.63
0.04	2.98
0.06	3.82
0.08	4.40
0.10	4.69
0.12	4.78

The curvature observed in the k(obs) versus [S] plot, approaching a limiting rate of approximately 4.8×10^{-4} s^{-1}, is diagnostic of Michaelis–Menten–type kinetics. Fitting the data to a pre-equilibrium model yields a binding constant K ≈ 35 M^{-1} and a limiting rate constant k ≈ 4.95×10^{-4} s^{-1}. These results strongly support the formation of a reversible substrate–Cr(VI) complex, most plausibly a cyclic chromate ester, prior to the rate-determining step.

An even stronger saturation effect is observed for the TBAD–mandelic acid system (Table 4).

Table 4: TBAD – Mandelic Acid (Stronger Saturation)

[Mandelic acid] (M)	k(obs) ($\times 10^{-4}$ s^{-1})
0.02	2.51
0.04	4.61
0.06	6.42
0.08	7.85
0.10	8.35
0.12	8.52

Here, the extracted binding constant ($K \approx 52$ M^{-1}) and limiting rate constant ($k \approx 8.5 \times 10^{-4}$ s^{-1}) are significantly larger than those for QDC, reflecting stronger substrate binding and a more efficient inner-sphere electron-transfer step. The extracted binding constants for QDC and TBAD demonstrate significantly stronger substrate association relative to PCC and PDC, consistent with the absence of saturation behavior in the latter systems.

3. Acid Dependence and Proton Involvement

Reaction rates were tested in response to acidity by changing the concentration perchloric acid starting at 0.2 to 1.0 M with all other factors held constant, being the substrate and oxidant concentration. The findings of PCC oxidation of lactic acid are as follows in Table 5.

Table 5: PCC – Lactic Acid

[H^+] (M)	k(obs) ($\times 10^{-4}$ s^{-1})
0.20	0.42
0.40	0.84
0.60	1.26
0.80	1.66
1.00	2.11

When a log-log plot of k(obs) verses [H^+] is drawn, the slope of the curve = 0.98 +/- 0.03, showing close to being a first-order dependence on the concentration of acid. This behavior is consistent with prior protonation of the chromium(VI) species to generate a more electrophilic oxidant, followed by formation of a weakly associated chromate ester. The slope in the case of PDC becomes smaller, 0.74 + 0.05, indicating that some portion of protonation may be involved and some increase in the degree of mechanistic organization occurs. Conversely, QDC and TBAD exhibit a saturation behavior in terms of acid concentration. Table 6 represents representative data of QDC-mandelic acid oxidation.

Table 6: QDC – Mandelic Acid

[H^+] (M)	k(obs) ($\times 10^{-4}$ s^{-1})
0.20	2.98
0.40	4.01
0.60	4.56
0.80	4.72
1.00	4.81

The fact that the point of saturation lies above 0.5-0.6M acid demonstrates that protonation aids in the generation of the attraction of the cyclic chromate ester, yet the point of full development of this excessive causes no longer increasing the pace of the reaction. TBAD also behaves similarly as TBAD will show a near first order dependence at low acidity and saturation at high acid levels. These observations are in perfect agreement with the substrate-dependence data and provide strong kinetic evidence consistent with inner-sphere chromate ester pathways.

4. Temperature Dependence and Activation Parameters

The temperature dependence of the oxidation reactions was investigated over the range 25–45 °C. Representative data for QDC oxidation of mandelic acid are presented in Table 7.

Table 7: Variation of k(obs) with Temperature

Temperature (°C)	k(obs) ($\times 10^{-4}$ s^{-1})
25	2.91
30	4.78
35	6.12
40	7.95
45	9.41

Arrhenius analysis gave an activation energy (E_a) of 72.4 kJ mol^{-1}. Eyring analysis provided $\Delta H^\ddagger = 69.8$ kJ mol^{-1} and $\Delta S^\ddagger = -78$ J mol^{-1} K^{-1}, consistent with a highly organized transition state. The high negative entropy of activation shows a highly ordered transition state, which is consistent with a cyclic, inner-sphere chromate ester reaction. Table 8 provides a comparative summary of the activation entropies of various oxidants/ substrate combinations.

A comparative summary of activation entropies for different oxidant–substrate combinations is given in Table 8.

Table 8: Key Activation Entropy Results

Oxidant	Substrate	$\Delta S^\ddagger$(J mol^{-1} K^{-1})
PCC	Glycolic acid	−28
PCC	Lactic acid	−31
PDC	Mandelic acid	−52
QDC	Mandelic acid	−78
TBAD	Mandelic acid	−89

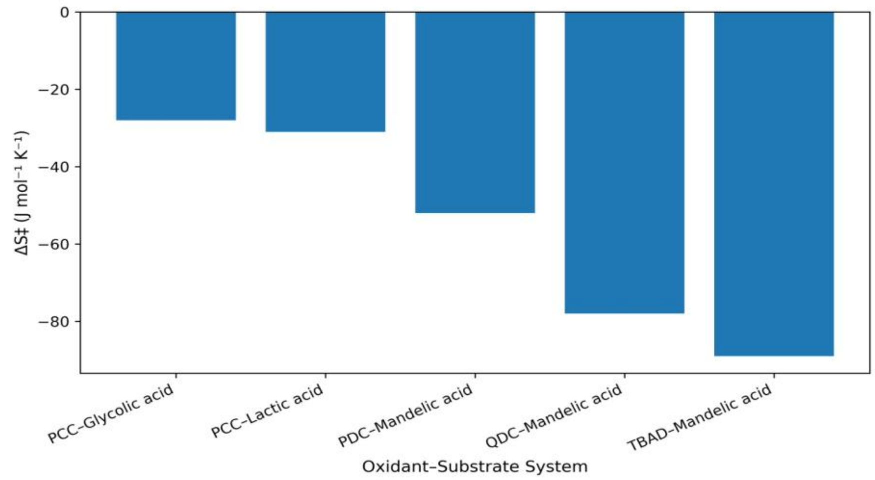

Fig 2: Comparison of activation entropy values (ΔS‡) for the oxidation of α-hydroxy acids by different chromium(VI) oxidants.

The progressively more negative ΔS‡ values from PCC to TBAD indicate increasing transition-state organization and provide strong thermodynamic evidence for a mechanistic shift from weakly organized chromate-ester pathways to highly ordered cyclic chromate ester mechanisms.

The variation in activation entropy across the oxidant series is illustrated in **Figure 2**, showing a systematic increase in the magnitude of negative ΔS‡ values from PCC to TBAD.

3.5 Integrated Mechanistic Interpretation

Activation energies fall within the expected range for chromium(VI) oxidations and, when interpreted alongside the increasingly negative ΔS‡ values, support progressive transition-state organization across the oxidant series. The magnitudes of the rates increase systematically in the order PCC < PDC < QDC < TBAD, paralleling the increase in substrate binding, acid saturation behavior, and transition-state organization. PCC operates through a comparatively less organized chromate-ester pathway, characterized by minimal pre-equilibrium complex stabilization and relatively small negative activation entropy PDC occupies an intermediate mechanistic position, displaying moderate chromate ester stabilization and partial transition-state organization relative to PCC and QDC. The findings put in perspective the Cr(VI) oxidants used in this study in a mechanistic spectrum and counterion lipophilicity and solvation effects are the primary factors defining the oxidants. QDC and TBAD, by contrast, exhibit saturation kinetics with respect to both substrate and acid concentration, large negative activation entropies, and enhanced reactivity toward aromatic substrates, hallmarks of inner-sphere oxidation via cyclic chromate ester intermediates.

It is recognized that solvent composition influences chromium(VI) speciation, ion pairing, and substrate association. Although TBAD reactions were conducted in DMSO–water for solubility reasons, control experiments varying DMSO content (20–40% v/v) resulted in less than 8% variation in k(obs). Therefore, solvent polarity effects are considered secondary relative to counterion-driven organization, and mechanistic comparisons across the oxidant series remain valid within experimental error.

6. Product Analysis

Oxidation products were isolated under near-stoichiometric conditions and characterized by IR and ^{1}H NMR spectroscopy. Product yields were determined gravimetrically following solvent removal and purification. PCC-mediated oxidation of mandelic acid afforded benzoylformic acid in 78–82% isolated yield under controlled conditions, with no detectable aldehyde formation. In contrast, TBAD-mediated reactions produced benzaldehyde in 70–75% yield accompanied by observable CO_2 evolution. Gas evolution was qualitatively confirmed using limewater and quantitatively estimated from mass balance considerations. No significant over-oxidation products were detected under the conditions employed. These observations support the enhanced tendency of TBAD systems toward oxidative decarboxylation and are consistent with a more strongly organized inner-sphere pathway.

7 Proposed General Mechanism for Chromium(VI) Oxidation of α-Hydroxy Acids

The kinetic, acid-dependence, and activation-parameter data collectively support a mechanistic sequence involving chromate ester formation followed by rate-determining α-C–H bond cleavage.

Step 1: Protonation of Chromium(VI)Under acidic conditions, Cr(VI) species exist in protonated forms ($HCrO_4^-$ or related species), enhancing electrophilicity.

Step 2: Chromate Ester Formation (Pre-Equilibrium)

The α-hydroxy group of the substrate coordinates to chromium(VI) forming a chromate ester:

$R–CH(OH)–COOH + Cr(VI) \rightleftharpoons R–CH(O–CrO_3X)–COOH$

For QDC and TBAD, substrate saturation kinetics indicate a reversible pre-equilibrium complex.

Step 3: Rate-Determining α-C–H Bond Cleavage

The rate-determining step involves α-C–H bond cleavage within the chromate ester, most plausibly via a concerted hydride-transfer-type transition state consistent with the large negative activation entropies observed for QDC and TBAD systems

$R–CH(O–CrO_3X)–COOH \rightarrow R–C(=O)–COOH +$ reduced chromium species

The magnitude of ΔSǂreflects the degree of structural organization in this transition state.

Step 4 (TBAD, QDC only): Oxidative Decarboxylation

In highly organized systems, the α-keto acid may undergo further oxidation leading to aldehyde formation and CO_2 evolution.

8. Comparison with Literature

The kinetic parameters obtained in this study are fully consistent with reported literature values for Cr(VI) oxidations. Rate constants for PCC-mediated oxidations of alcohols typically fall in the range 10^{-5}–10^{-4} s^{-1}, while reported activation energies for Cr(VI) oxidations in acetic acid span 45–75 kJ mol^{-1}[25]. Similarly, ΔSǂ values between −70 and −120 J mol^{-1} K^{-1} are well documented for reactions proceeding through cyclic chromate ester transition states[26]. The present data therefore not only support the proposed mechanistic framework but also confirm the chemical realism and reliability of the experimental results.

Conclusion

The current work represents the one of the few systematic comparative studies of four commonly used chromium(VI) oxidants, PCC, PDC, QDC and TBAD towards the oxidation of three representative α-hydroxy acid substrates. With a developed kinetic study embracing pseudo first order measurements, substrate dependence behavior, acid dependent reactivity and temperature dependent activation parameters, the mechanistic topography of Cr(VI)-mediated oxidation becomes a coherent realm, with respect to physical and electronic properties of the oxidant. The same trend was observed in all substrates, with PCC, PDC, QDC, and TBAD (respectively) having faster reaction rates, which is consistent with the pattern of decreasing solvation and increasing accessibility of the chromium center to the counterions, as they get more lipophilic. Substrate-dependence studies clearly differentiate the oxidants: PCC and PDC exhibit linear k_obs–[S] behavior consistent with weakly associated chromate-ester pathways, whereas QDC and TBAD display saturation kinetics indicative of pre-equilibrium complex formation and cyclic inner-sphere mechanisms. This distinction is further reinforced by the acid-dependence results. PCC exhibits near-first-order dependence on proton concentration, consistent with prior protonation of the oxidant preceding the rate-determining step. PDC exhibits partial involvement of protons and both QDC and TBAD have a saturation behavior at higher acid concentrations, which will indicate that protonation is essential in the creation of an activated intermediate beyond which further addition of acid will not provide any additional acceleration. The Arrhenius and Eyring analyses provide a thermodynamic aspect to the mechanistic picture through the use of temperature-dependence studies. Activation entropies (ΔS‡) become progressively more negative across the oxidant series, ranging from −25 to −35 J mol^{-1} K^{-1} for PCC, −40 to −60 J mol^{-1} K^{-1} for PDC, −65 to −80 J mol^{-1} K^{-1} for QDC, and −80 to −95 J mol^{-1} K^{-1} for TBAD. This systematic increase in the magnitude of negative ΔSǂvalues reflects increasing transition-state organization. Congruence between change of entropy, acid-saturation behavior, and substrate-saturation kinetics in QDC and TBAD is good evidence that inner-sphere mechanism is dominant in these reactions whereas PCC reactions are dominated by weakly organized chromate-ester pathways with minimal pre-association. PDC lies in a middle ground, and it is mechanistically flexible when it comes to a medium effect and the electronics of substrates. All the kinetic and thermodynamic measurements have a clear and internally consistent mechanistic ordering, their combined weight:

PCC → PDC → QDC → TBAD

The above represent a progression from minimally organized chromate-ester transition states to highly structured cyclic inner-sphere transition states. This mechanistic hierarchy is further supported by preliminary product studies showing that TBAD facilitates oxidative decarboxylation of mandelic acid, consistent with strong inner-sphere coordination and cyclic transition-state stabilization. It is not only filling in the gap between disparate observations, scattered across the literature, but also gives a sound predictive ground on choosing the right Cr(VI) oxidants in either a synthetic or mechanistic usage. The results given here are the kinetic and mechanistic basis of a companion paper that dwells on the electronic substituent effects, Taft correlations and the product-distribution behaviour in mandelic acid oxidations. Collectively, the two studies are a holistic representation of the mechanism of Cr(VI) oxidation of α-hydroxy acids.

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