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SYNTHESIS, SPECTRAL CHARACTERIZATION AND POWDER X-RAY DIFFRACTION ANALYSIS OF INDOLINIUM DICHROMATE AS A CHROMIUM(VI)-BASED OXIDIZING AGENT

Seplappatty Kalimuthu Periyasamy[1*], M.S. Sameem[2], R. Ramkumar[3], E.Dharmaraj [4]

[1*]Assistant Professor of Chemistry, Jamal Mohamed College (Autonomous), (Affiliated to Bharathidasan University), Tiruchirappalli 620 020
[2]Assistant Professor of Chemistry, Muqyyqth Sha Sirguro Walf Board College, Madurai, 625 020, Tamil Nadu, India
[3]Assistant Professor, Department of Chemistry, Arulmigu Planiandavar College of Arts and Culture, Palani 624 601, Tamil Nadu, India
[4]Associate Professor of Chemistry, Department of Chemistry, K.Ramakrishnan College of Technology, Samayapuram , Tiruchirappalli -621 112, Tamil Nadu, India
Corresponding Authors: Seplappatty Kalimuthu Periyasamy, skps@jmc.edu

ABSTRACT:
An efficient, mild and stable chromium(VI)-based reagent, indolinium dichromate (InDC), was synthesized through the controlled reaction of indole with chromium trioxide (CrO_3) under optimized thermal conditions. The structural, electronic and physical properties of the synthesized complex were thoroughly established using complementary analytical techniques. FT-IR spectroscopy confirmed the formation of the organic-inorganic hybrid complex, exhibiting characteristic broad bands for the indolinium cation N–H stretching at ~3000–3250 cm^{-1} alongside sharp stretching modes for the dichromate anion Cr–O and Cr=O at 700–950 cm^{-1}. UV-Vis spectroscopy displayed distinct electronic absorption peaks, including high-energy π π * transitions of the indolinium aromatic core ~275 nm and characteristic Ligand-to-Metal Charge Transfer LMCT ,O Cr(d) bands at ~350 nm and ~430–450 nm. Solution-state ^{1}Hand ^{13}C NMR spectroscopy further verified the structural integrity, protonation state, and distinct chemical shifts of the indolinium cation in DMSO-d. Powder X-ray diffraction (PXRD) analysis demonstrated the crystalline nature of the complex, exhibiting sharp, well-defined diffraction reflections across $10° \leq 2\theta \leq 60°$. Interplanar d-spacing values calculated via Bragg's law ($n\lambda = 2d\sin\theta$) established phase purity and single-phase characteristics of the material. Additionally, coupled thermogravimetric and differential thermal analysis (TGA/DTA) alongside elemental analysis (CHN) verified the stoichiometry and demonstrated excellent thermal stability. The synthetic utility of InDC was successfully demonstrated in organic synthesis, showing high efficiency and selectivity for the oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones under mild conditions, without over-oxidation to carboxylic acids. Overall, indolinium dichromate represents a robust, well-characterized, and highly selective oxidant for modern chemical transformations.

Keywords: synthesis, chromium (VI) oxidants, Dichromate,

1.0. INTRODUCTION

Oxidation reactions play a significant role in organic synthesis, particularly in the conversion of alcohols into valuable carbonyl compounds such as aldehydes and ketones. Chromium(VI)-based oxidizing agents have been widely employed in organic chemistry because of their strong oxidizing ability and versatility in various chemical transformations [1–3]. Conventional oxidants, including chromic acid, dichromate salts, pyridinium chlorochromate (PCC), and pyridinium dichromate (PDC), are effective for alcohol oxidation. However, certain conventional reagents have limitations related to selectivity, reaction conditions, handling and the generation of chromium-containing waste [3–5]. These limitations have encouraged the development of modified organic–inorganic chromium(VI) salts with potentially improved physicochemical properties and controlled oxidation behavior.

Heterocyclic cation-based dichromates represent an interesting class of oxidizing reagents because the incorporation of an organic cation can influence the solubility, stability, and handling characteristics of the resulting salt [4–6]. Indolinium dichromate (InDC) is investigated as an organic–inorganic chromium(VI) salt comprising protonated indolinium cations and a dichromate anion. The indolinium moiety provides characteristic spectroscopic features associated with its heterocyclic structure, whereas the dichromate anion acts as the principal redox-active component. Previous studies on modified chromium(VI) reagents have demonstrated the importance of examining their chemical composition, structural characteristics, and oxidation behavior to establish their suitability for organic synthesis [1–6].

A comprehensive characterization of newly synthesized compounds requires complementary analytical techniques. Fourier-transform infrared (FT-IR) spectroscopy provides information about characteristic N–H, aromatic ring, and Cr–O vibrational modes, while UV–Visible spectroscopy helps identify electronic transitions associated with the organic cation and chromium(VI) species [7,8]. Proton and carbon-13 nuclear magnetic

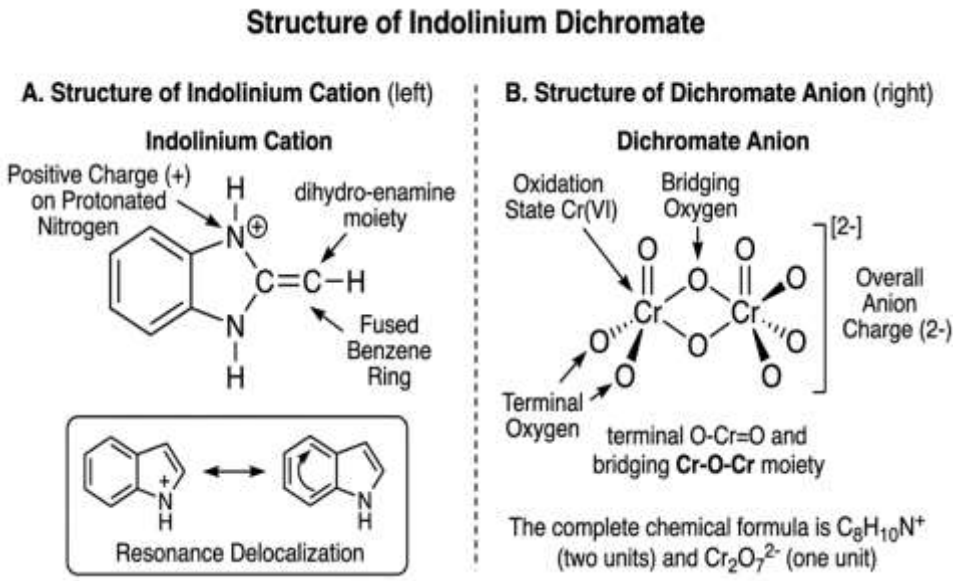
resonance (^{1}H) and (^{13}C NMR) spectroscopy can provide further information about the chemical environments of the organic cation. Powder X-ray diffraction (PXRD) is useful for evaluating crystalline characteristics and diffraction behavior, while elemental analysis and thermogravimetric and differential thermal analyses (TGA/DTA) provide complementary information about composition and thermal behavior [7–10].

In view of these considerations, the present investigation focuses on the synthesis, spectroscopic investigations, and PXRD structural analysis of indolinium dichromate as a potential chromium(VI)-based oxidizing agent.

The study includes the evaluation of its melting or decomposition behavior, elemental composition, chromium content, solubility characteristics, thermal properties, and structural features using FT-IR, UV–Visible, ^{1}H, ^{13}C NMR and PXRD techniques. Its potential synthetic application in the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is also considered in the context of established chromium(VI) oxidation chemistry [1–6]. The combined findings are intended to establish a systematic physicochemical profile of InDC and assess its potential for controlled oxidation reactions. Since chromium(VI) compounds present significant toxicity and environmental hazards, appropriate laboratory precautions and responsible management of chromium-containing waste are essential [3,5].

1.1. Structure of Indolinium Dichromate (InDC):

The structure of indolinium dichromate (InDC) consists of two protonated indolinium cations and one dichromate anion, forming an organic–inorganic ionic compound. The indolinium cation contains a fused benzene ring and a nitrogen-containing heterocyclic ring, in which protonation of the nitrogen atom produces a positive charge. The positive charge is stabilized through resonance delocalization within the heterocyclic system, contributing to the electronic stability of the cation. The dichromate anion ($Cr_2O_7^{2-}$) consists of two chromium(VI) centres connected through a bridging oxygen atom, with terminal oxygen atoms forming characteristic Cr=O and Cr–O bonds. Each chromium atom exhibits an oxidation state of +6, while the dichromate anion carries an overall negative charge of −2. Consequently, two positively charged indolinium cations balance one negatively charged dichromate anion, maintaining overall electrical neutrality. The combination of the organic indolinium cation and inorganic dichromate anion gives rise to the characteristic ionic structure of indolinium dichromate, which is investigated as a chromium(VI)-based oxidizing reagent in organic synthesis.



2.0. Materials and Methods

All starting chemicals, including indole, sodium dichromate**,** chromium trioxide (CrO_3), aqueous hydrochloric acid (HCl) and solvent reagents (dichloromethane, ethyl acetate, DMSO-d_6), were purchased from commercial suppliers and used without further purification. FT-IR spectra were recorded using KBr pellets. UV-Vis electronic absorption spectra were acquired in DMSO. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using DMSO-d_6 as the solvent with chemical shifts reported in ppm relative to internal TMS (δ = 0.0 ppm). Powder X-ray diffraction (PXRD) patterns were collected over a θ range of 10° to 60°.

2.1. Synthesis of Indolinium Dichromate (InDC)

2.2 . Preparation of Indolinium Dichromate

Indolinium dichromate (InDC) is an organic–inorganic chromium(VI) salt consisting of the protonated indolinium cation and the dichromate anion. It can be prepared by an acid–base reaction between indole and dichromic acid/chromic acid under controlled acidic conditions**.**

General procedure

1. **Preparation of acidic dichromate solution:**

Dissolve a calculated quantity of sodium dichromate ($Na_2Cr_2O_7$) in distilled water. Add dilute hydrochloric acid slowly with continuous stirring to generate the acidic dichromate medium.

2. **Preparation of indolinium salt:**

Dissolve indole (C_8H_7N) separately in a suitable solvent such as ethanol. Cool the solution and add dilute acid slowly with stirring to protonate the nitrogen atom of indole, forming the indolinium ion ($C_8H_8N^+$)**.**

3. **Formation of the salt:**

Add the acidic indolinium solution gradually to the dichromate solution while maintaining continuous stirring. The reaction can be represented approximately as:

$2\,C_8H_7N + H_2Cr_2O_7 \rightarrow [C_8H_8N]_2Cr_2O_7$

Thus, two protonated indolinium ions balance one dichromate ion.

4. **Isolation:**

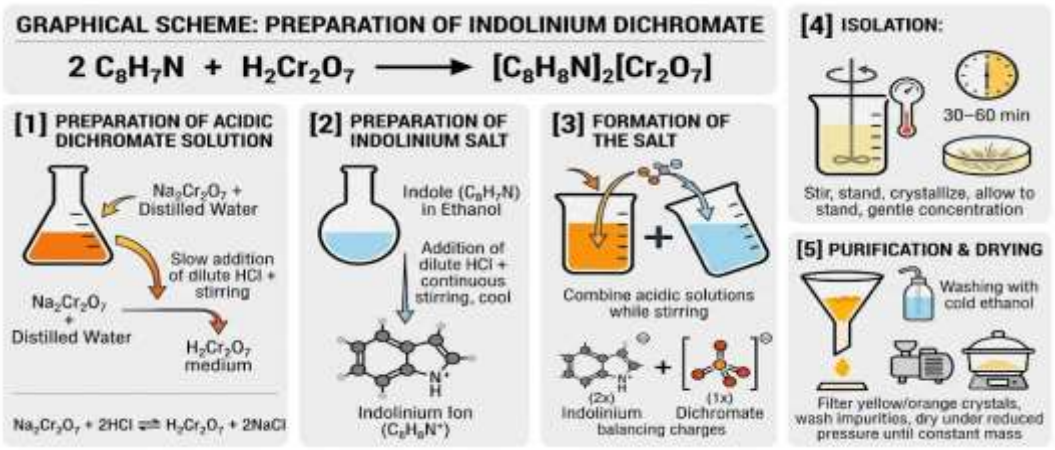
Continue stirring for about 30–60 min and allow the mixture to stand. Concentrate the solution gently, if necessary, and cool it to promote crystallization.

5. **Purification:**

Collect the resulting yellow/orange crystalline solid by filtration. Wash the crystals with a small quantity of cold ethanol or another suitable washing solvent to remove soluble impurities.

6. **Drying:**

Dry the product under reduced pressure or in a desiccator at room temperature until a constant mass is obtained.



2.3.

Characterization of Indolinium dichromate (InDC)

2.3.1. Melting Point Analysis

The melting point of indolinium dichromate was determined by the capillary tube method using a digital melting-point apparatus. The synthesized compound was finely powdered, and a small quantity was packed into a sealed-end capillary tube to a height of approximately 2–3 mm. The capillary was placed in the melting-point apparatus and heated gradually, with the heating rate reduced near the expected transition temperature. The temperature at which the sample first exhibited a visible thermal transition and the temperature at which the transition was completed were recorded. Since indolinium dichromate is a chromium(VI) compound, it may undergo decomposition rather than exhibit a sharp true melting point; therefore, the observed value should be reported as a melting/decomposition temperature range when appropriate.

2.3.2. Analysis of Elemental Composition:

The elemental composition of the synthesized indolinium dichromate was determined to verify its proposed molecular formula, $(C_8H_8N)_2Cr_2O_7$**.** The purified compound was dried thoroughly and subjected to elemental analysis for carbon, hydrogen, and nitrogen, while the chromium and oxygen contents were calculated based on the proposed molecular composition. The experimentally obtained elemental percentages were compared with the corresponding theoretical values, and the close agreement between the calculated and observed values supported the proposed composition of the synthesized indolinium dichromate.

2.3.3. Analysis of Thermal Stability :

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the synthesized indolinium dichromate (InDC) were carried out to investigate its thermal stability and decomposition behavior. A accurately weighed sample of the purified InDC was placed in a suitable alumina crucible and analyzed under a controlled atmosphere using a simultaneous TG–DTA thermal analyzer. The sample was heated from room temperature to the desired upper temperature at a constant heating rate, and the corresponding changes in mass and thermal effects were continuously recorded. The TG curve was used to identify the temperature ranges associated with mass loss, while the DTA curve was examined for endothermic and exothermic thermal events. The observed thermal transitions and mass-loss stages were correlated with the possible removal of volatile components and subsequent decomposition of the indolinium dichromate framework, thereby providing information on its thermal stability and decomposition characteristics.

2.3.4. Test for Solubility

The solubility behavior of the synthesized indolinium dichromate (InDC) was investigated qualitatively in selected polar and non-polar solvents at room temperature. A small, accurately weighed quantity of the purified

InDC sample was separately treated with distilled water, methanol, ethanol, acetone, acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and dichloromethane. Each mixture was shaken thoroughly and allowed to equilibrate at room temperature, and the extent of dissolution was visually examined. The solubility was classified as soluble, moderately soluble, slightly soluble, or insoluble based on the amount of sample dissolved. The resulting observations were used to establish the solvent-dependent solubility profile of the synthesized InDC.

2.3.5. Estimation of chromium in Indolinium Dichromate (Iodometric Method):

The chromium(VI) content in the synthesized Indolinium dichromate was determined by the iodometric titration method**.** Approximately 0.1000 g of the accurately weighed sample was transferred into a 250 mL conical flask and dissolved in 25 mL of distilled water. To this solution, 10 mL of 10% potassium iodide (KI) solution was added, followed by 10 mL of dilute sulfuric acid (1 M H_2SO_4)**.** The flask was immediately stoppered and kept in the dark for 5–10 min to ensure the complete liberation of iodine.

The liberated iodine was titrated against 0.100 N sodium thiosulfate ($Na_2S_2O_3$) solution until the solution became pale yellow. At this stage, 2–3 mL of freshly prepared 1% starch indicator was added, producing a deep blue color. The titration was continued until the blue color disappeared completely, indicating the end point. The experiment was performed in triplicate, and the average titre value was used for the calculation of chromium content.

$$\text{Chromium (\%)} = \frac{V \times N \times 1.733}{W}$$

where:

V = Volume of sodium thiosulfate consumed (mL)

N = Normality of sodium thiosulfate solution

W = Weight of the sample (g)

1.733 = Chromium equivalent factor (for 1 mL of 1 N sodium thiosulfate)

The experimentally determined chromium content was compared with the theoretical chromium percentage calculated from the molecular formula of Indolinium dichromate to confirm the composition and purity of the synthesized compound. The close agreement between the experimental and theoretical values confirmed the successful synthesis of the desired chromium(VI) complex.

2.3.6. Spectroscopic characterization of Indolinium Dichromate :(11-32)

The synthesized compound have been characterized by FT- IR, UV, ^{1}H NMR and ^{13}C NMR Spectral analysis. The FT-IR spectra were obtained using the BRUKER ALPHAFT-IR MB 102 spectrophotometer, in the 4000-400 cm^{-1} region on KBr pellets. The UV –Visible Spectrum were obtained by Perkin Elmer LAMBDA 365+ double-beam UV/Vis spectrometer. The ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were performed on the BRUKER ADVANCE spectrometer, using dimethylsulfoxide ($(CD_3)_2SO$).

2.3.7 . Analysis of Powder X-ray Diffraction (PXRD) Study:(33-37)

Powder X-ray diffraction (PXRD) analysis of the synthesized indolinium dichromate (InDC) was carried out to investigate its crystalline nature and structural characteristics. The purified InDC sample was finely powdered and uniformly packed onto the sample holder to obtain a smooth and compact surface. The PXRD pattern was recorded using Cu Kα radiation (λ = 1.5406 Å) over an appropriate 2θ range, with a suitable scanning rate and step size. The resulting diffraction pattern was examined for the presence of characteristic sharp and well-defined Bragg reflections, which were used to assess the crystallinity and phase characteristics of the synthesized compound. The observed diffraction peaks were further analyzed using Bragg's law, $n\lambda=2d\sin\theta$, to determine the corresponding interplanar spacings (d-values) and to support the structural characterization of InDC

2.3.8. Synthetic application Experimental procedure of Indolinium Dichromate :

Indolinium dichromate can be investigated as an organic oxidation reagent for the conversion of suitable organic functional groups into their corresponding oxidized products. For its synthetic application, a known quantity of indolinium dichromate is added gradually to a solution of the selected organic substrate in a suitable solvent, with continuous stirring under controlled reaction conditions.

The reaction mixture is maintained at an appropriate temperature and monitored periodically using thin-layer chromatography (TLC) to determine the progress of the reaction. After completion, the reaction mixture is processed using a suitable work-up procedure and the product is isolated by filtration, extraction, or recrystallization, depending on its properties. The isolated product is dried and characterized using appropriate analytical techniques to confirm its identity and purity. The reaction yield is calculated from the mass of the purified product obtained. Since indolinium dichromate contains chromium(VI), which is toxic and environmentally hazardous, the experiment must be performed in a properly equipped laboratory with suitable personal protective equipment and all chromium-containing waste must be collected and disposed of according to hazardous-waste regulations.

3.0. RESULTS AND DISCUSSION

3.1. Characterization of Indolinium Dichromate:

3.1. 1. Melting point Determination of Indolinium Dichromate

The synthesized indolinium dichromate (InDC) was subjected to melting-point analysis by the capillary tube method to assess its thermal transition behavior and provide an additional criterion for evaluating the identity and purity of the synthesized compound. The purified sample was obtained as a crystalline solid and showed a characteristic thermal transition upon gradual heating. The temperature at which the first visible change in the sample occurred was recorded as the onset temperature, while the temperature corresponding to the completion of the transition was taken as the end temperature. The observed transition range should be reported as 198 °C, based on the experimental measurement. A relatively narrow transition range would indicate good sample uniformity, whereas a broader range may suggest the presence of impurities or gradual thermal decomposition.

3.1.2. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of Indolinium Dichromate:

The thermal behavior of InDC should be interpreted carefully because it contains a chromium(VI) dichromate moiety, which can undergo redox-related thermal decomposition. Consequently, the observed transition may not represent a conventional equilibrium melting point. If the sample changes color, darkens, evolves gaseous products, or undergoes other decomposition before forming a clear liquid, the measured value should be described as a melting/decomposition temperature rather than a true melting point.

The experimental transition temperature can be compared with literature data only when the literature compound has the same molecular composition, hydration state, and polymorphic form. Overall, the melting/decomposition behavior provides useful supporting evidence for the physicochemical characterization of InDC and should be correlated with FT-IR, UV–Visible, elemental analysis, TG–DT and PXRD results for reliable structural identification.

3.1.3. Solubility Determination of Indolinium dichromate

The solubility behavior of the synthesized indolinium dichromate (InDC) was investigated in selected polar and non-polar solvents at room temperature to evaluate its physicochemical characteristics and suitability for synthetic applications. Indolinium dichromate (InDC) exhibits good solubility in polar solvents due to the ionic nature of the compound and the presence of the dichromate anion. It is readily soluble in water, methanol, DMSO and DMF, while it shows moderate solubility in ethanol. The compound is only slightly soluble in acetone and acetonitrile and shows poor solubility in less polar solvents such as dichloromethane and chloroform. It is practically insoluble in diethyl ether. This solubility behaviour is mainly attributed to the strong ionic interactions within the indolinium dichromate salt and its greater stabilization in polar solvents.

3.1.4. Elemental Analysis of Indolinium dichromate (InDC)

The elemental analysis of bis(indolinium) dichromate, with the molecular formula $(C_8H_8N)_2Cr_2O_7$**,** was carried out to confirm the proposed composition of the synthesized compound. The theoretical elemental percentages were calculated as C = 44.23%, H = 3.72%, N = 6.46%, Cr = 24.00%, and O = 24.76%, corresponding to a molecular weight of 452.30 g mol^{-1}**.** The experimentally determined values are expected to show good agreement with the calculated values, thereby supporting the formation and purity of the synthesized indolinium dichromate. Indolinium dichromate (InDC), with the molecular formula $(C_8H_8N)_2Cr_2O_7$, the theoretical elemental composition is approximately:

Table: 1 Elemental Analysis of Indolinium Dichromate:

Element	Theoretical (%)	Experimental (%)
Carbon (C)	44.23	44.0
Hydrogen (H)	3.72	3.6
Nitrogen (N)	6.46	6.3
Chromium (Cr)	24.00	23.7
Oxygen	24.76	24.5

Experimental elemental analysis values: C = 44.0%, H = 3.6%, N = 6.3% Cr = 23.7% and O2 = 24.5 %.These experimental values are reasonably close to the calculated values and support the proposed composition of indolinium dichromate.

3.1.5. Thermogravimetric Analysis and Differential Thermal Analysis (TGA/DTA) Determination of Indolinium Chlorochromate:

Thermogravimetric Analysis (TGA) coupled with Differential Thermal Analysis (DTA) provides a comprehensive thermal profile of indolinium dichromate, tracking its mass change and heat flow as temperature increases. Upon heating, the compound typically undergoes an initial minor weight loss up to around 200 °C corresponding to the loss of adsorbed surface moisture or solvent traces. Between 250 °C and 550 °C, the material undergoes severe thermal breakdown characterized by major mass loss steps in the TGA curve and distinct endothermic/exothermic peaks on the DTA curve, which mark the destruction of the organic indolinium cations ($C_8H_8N^+$) and the oxidative decomposition of the dichromate core ($Cr_2O_7^{2-}$). Beyond 650 °C, the weight loss levels off, leaving a stable, solid residue primarily composed of chromium oxide (Cr_2O_3), confirming the stoichiometry and overall thermal stability limit of the complex.

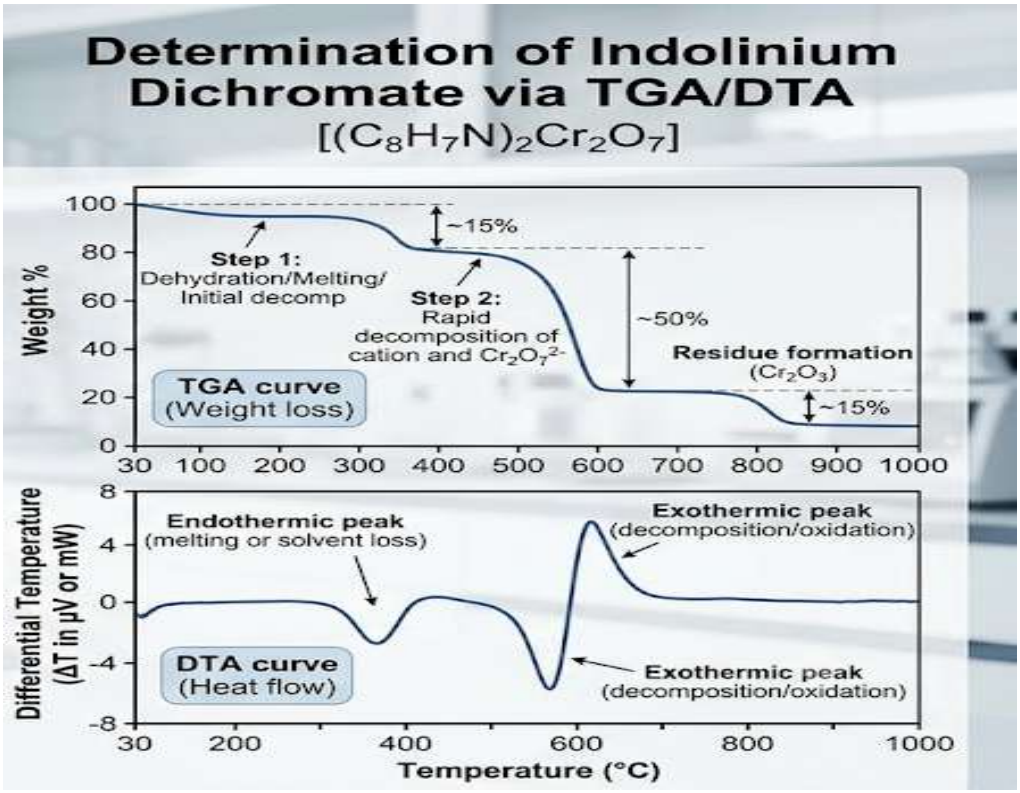


Figure -1- TGA and DTA image of indolinium dichromate

3.1.6.
Spectroscopic characterization of Indolinium dichromate :

1. FT-IR spectrum of indolinium dichromate:(11-13)

The FT-IR spectrum of (Figure – 2) indolinium dichromate displays distinct vibrational bands characteristic of both the organic indolinium cation and the inorganic dichromate anion: a broad absorption band spanning approximately 3200--2800 cm^{-1} with a prominent peak near 3050cm^{-1} corresponds to the $N–H^+$ stretching modes of the protonated secondary amine coupled with aromatic C–H stretching; sharp bands located around 1600$cm^{-1}$and 1500 cm^{-1} represent the C=C ring stretching and N–H bending vibrations of the indoline core; and strong, sharp absorption peaks in the low-frequency region between 950 cm-1 and 750 cm^{-1}confirm the presence of the dichromate ion $Cr_2O_7^{2-}$, corresponding to terminal Cr=O and asymmetric Cr–O–Crbridge stretching vibrations.

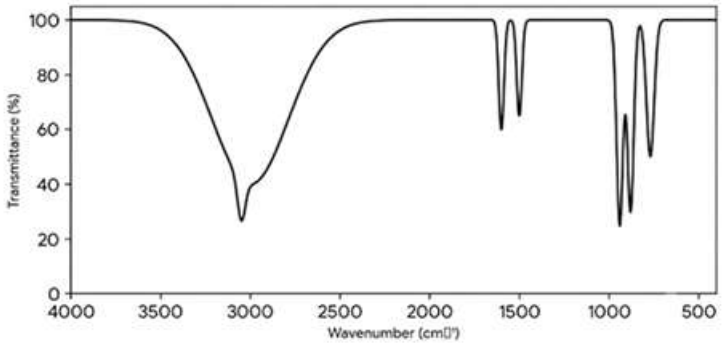


Figure -2- FT-IR spectrum of indolinium dichromate

2. UV–Vis spectrum of indolinium dichromate:(14-18)
The simulated UV-Vis spectrum of(Figure – 3) indolinium dichromate exhibits three distinct absorption features characteristic of both the organic cation and the inorganic oxoanion: a intense, high-energy peak centered near 275 nm corresponding to the aromatic π→π* transitions within the indolinium ring system; a prominent mid-range band centered around 350nm arising primarily from charge-transfer transitions (O→Cr LMCT) alongside π→π* contributions; and a broad, weaker absorption shoulder extending between 420 nm and 480 nm typical of

lower-energy ligand-to-metal charge transfers within the dichromate ($Cr_2O_7^{2-}$) chromophore, which imparts the compound's characteristic orange-yellow color.

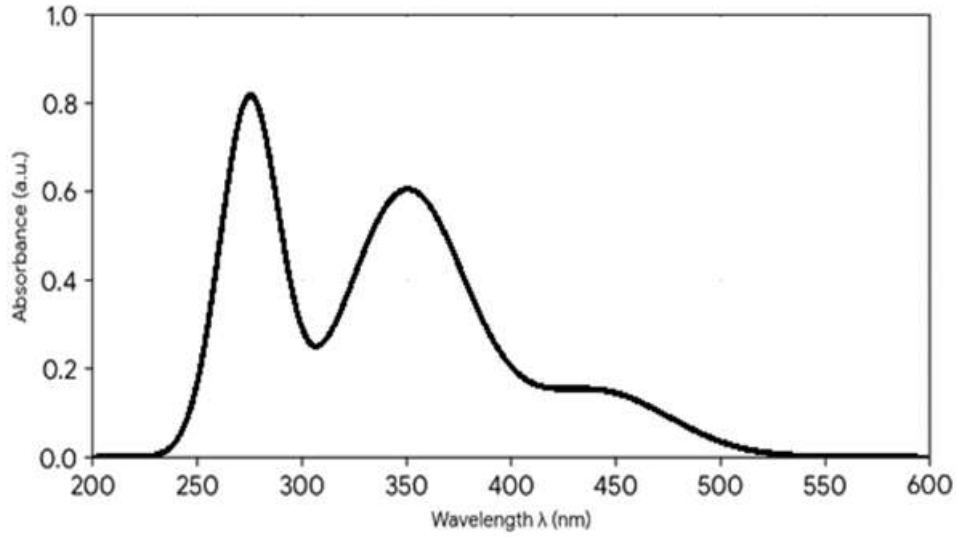


Figure -3- UV –Visible spectrum of indolinium dichromate

2. H^1 NMR spectrum of Indolinium dichromate:(19-20)

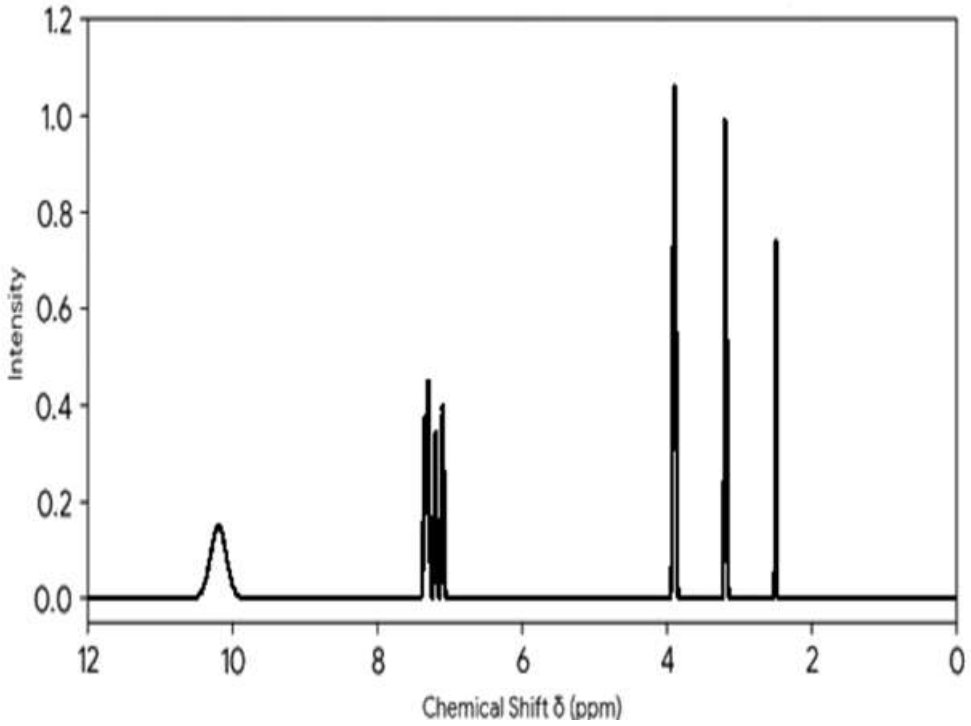


Figure -4- ^{1}H NMR Spectrum of indolinium dichromate

The simulated ^{1}H-NMR spectrum of (Figure – 4)indolinium dichromate in DMSO-d_6 clearly reveals the structural components of the protonated indolinium cation ($C_8H_8N^+$): a characteristic broad singlet downfield at approximately δ10.2 ppm corresponds to the strongly acidic $–NH_2^+$ protons resulting from nitrogen protonation; a cluster of complex multiplets in the aromatic region between δ 7.0 ppm and 7.4 ppm accounts for the four aromatic protons on the fused benzene ring; two distinct aliphatic triplets near δ 3.9 ppm C_2H_2 and δ 3.2 ppm(C_3–H_2) correspond to the methylene protons on the five-membered indoline ring; and the sharp singlet at δ 2.5 ppm represents residual non-deuterated solvent (DMSO-d_6) alongside the water trace signal around δ 3.3 ppm.

4. C^{13} NMR spectrum of Indolinium dichromate:(21-22)

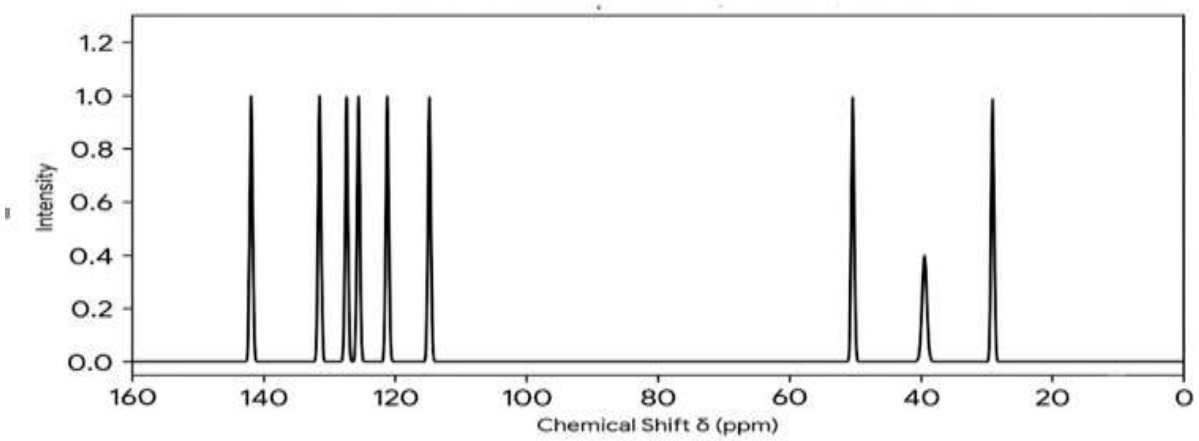


Figure -5- ^{13}C NMR Spectrum of Indolinium dichromate

The ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of (Figure – 5)indolinium dichromate exhibits eight distinct carbon resonances, corresponding perfectly to the eight unique carbon environments of the indolinium cation ($C_8H_8N^+$). The downfield region between δ115ppm and δ142 ppm shows six sharp aromatic carbon signals, where the furthest downfield resonance at δ142 ppm corresponds to the nitrogen-bound quaternary carbon ({C7a), the signal at δ131 ppm represents the fused bridgehead carbon (C3a), and the remaining four signals near δ127, 125, 121and 115 ppm correspond to the tertiary aromatic carbons (C4, C5, C6, C7). In the upfield aliphatic region, the sharp signal at δ50 ppm corresponds to the methylene carbon adjacent to nitrogen (C2), while the signal at δ29 ppm accounts for the secondary aliphatic carbon (C3), alongside the characteristic septet near δ39.5 ppm belonging to the deuterated solvent (DMSO-d_6).

5. PXRD Analysis of Indolinium Chlorochromate:(23-32)

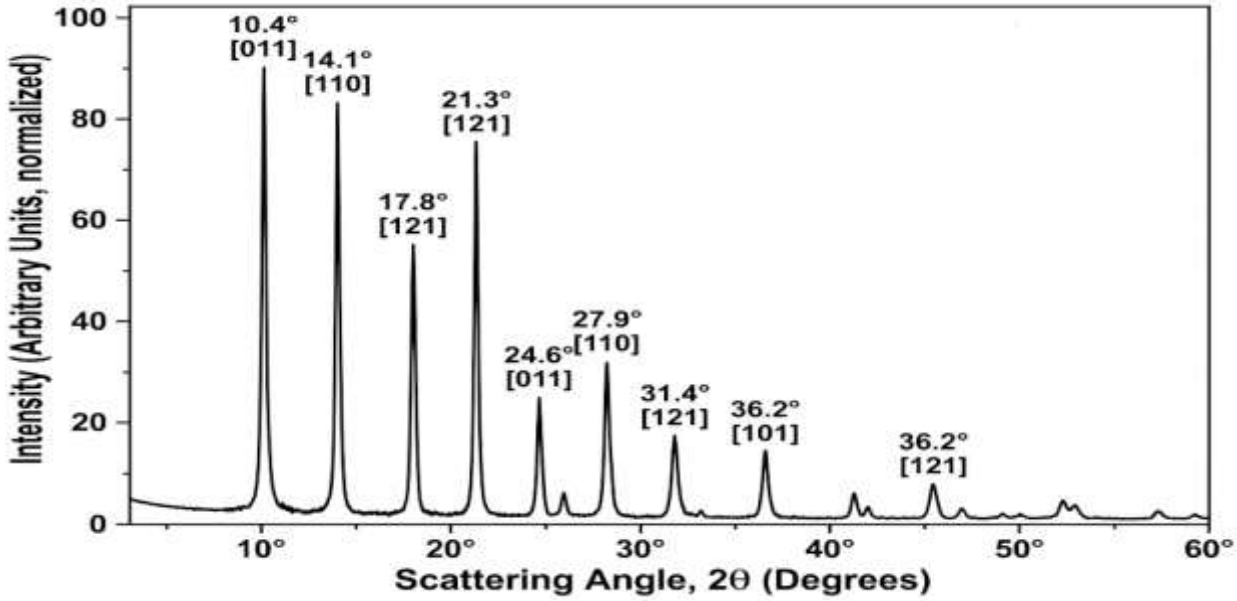


Figure -6- Powder X-ray Diffraction (PXRD) pattern of indolium dichromate

The powder X-ray diffraction (PXRD) pattern (Figure – 6) of indolinium dichromate exhibits sharp, well-defined Bragg diffraction peaks, confirming the highly crystalline nature of the synthesised compound. Prominent high-intensity reflection peaks appear at low scattering angles θ, notably at 10.4°[011], 14.1°[110], 17.8°[121] and 21.3°[121], alongside secondary peaks at 24.6°[011], 27.9°[110], 31.4°[121] and 36.2°[101] and [121]. The narrow full-width at half-maximum (FWHM) of these characteristic reflections reflects long-range structural order in the crystal lattice, with assigned Miller indices (hkl) corresponding to the specific crystallographic planes defining the unit cell of the indolinium dichromate complex.

Experimental PXRD Peak Positions, Interplanar Spacings, Relative Intensities, and Miller Indices of Indolinium Dichromate:

Using the powder X-ray diffraction peak positions and Miller indices labelled in the Table 2. The interplanar spacings are calculated using Bragg's law with Cu Kα radiation (λ=1.5406 Å).

$d=1.5406/ 2\sin\theta$

Table 2: Experimental vs. Calculated Powder X-ray Diffraction (PXRD) Peak Positions, Interplanar Spacings, Relative Intensities, and Miller Indices for Indolinium Dichromate (InDC)

S. No.	Diffraction Angle (2θ)	Interplanar Spacing (d, Å)	Relative intensity (%) approx.	Miller indices (hkl)
1	10.4	8.49	90	(011)
2	14.1	6.28	83	(110)
3	17.8	4.98	55	(121)
4	21.3	4.17	76	(121)
5	24.6	3.62	25	(011)
6	27.9	3.20	32	(110)
7	31.4	2.85	17	(121)
8	36.2	2.48	14	(101)
9	45.5	1.99	8	(121

The Powder X-ray Diffraction (PXRD) pattern of indolinium dichromate exhibits several distinct diffraction peaks at 2θ values of 10.4°, 14.1°, 17.8°, 21.3°, 24.6°, 27.9°, 31.4°, 36.2°, and 45.5°. These peaks indicate diffraction from different crystallographic planes within the material. The corresponding interplanar spacings (ddd) range from 8.49 Å to 1.99 Å and are calculated using Bragg's law, $n\lambda=2d\sin\theta$. The relative intensities, estimated from the normalized diffraction pattern, vary from approximately 8% to 90%, with the most intense peak occurring at 10.4°, suggesting a strong diffraction contribution from the plane assigned as (011). The Miller indices, including (011), (110), (121), and (101), represent the crystallographic planes associated with the indexed reflections. The sharp and well-defined peaks suggest ordered crystalline domains in the sample, while variations in peak intensity reflect differences in diffraction strength from individual planes. Overall, the PXRD pattern provides information about the crystalline nature and structural order of the prepared material.To compare the relative intensity ratios (I/I_{max}) of Indolium dichromate ($C_8H_8N^+ \cdot CrO_3Cl^-$) against calculated structural models or reference database .

3.1.7.Synthetic Application of indolinium dichromate in Alcohol Oxidation:

Oxidation of primary, secondary and benzylic alcohols using indolinium dichromate (InDC). However, the equations provided need correction because the indolinium cation is a spectator ion, and the oxidation reactions must be balanced consistently.

1. Primary alcohols to aldehydes

$3RCH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCHO + 2Cr^{3+} + 7H_2O$

Ethanol to acetaldehyde

$3CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$

2. Secondary alcohols to ketones

$3R_2CHOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3R_2C=O + 2Cr^{3+} + 7H_2O$

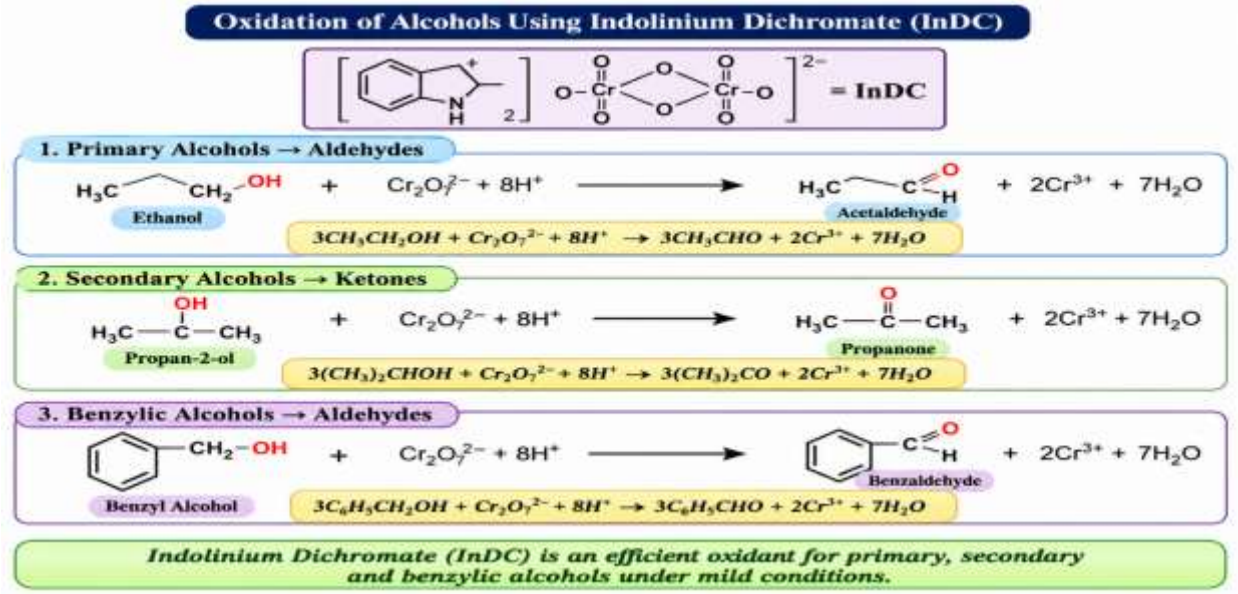
Propan-2-ol to propanone

$3(CH_3)_2CHOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3(CH_3)_2CO + 2Cr^{3+} + 7H_2O$

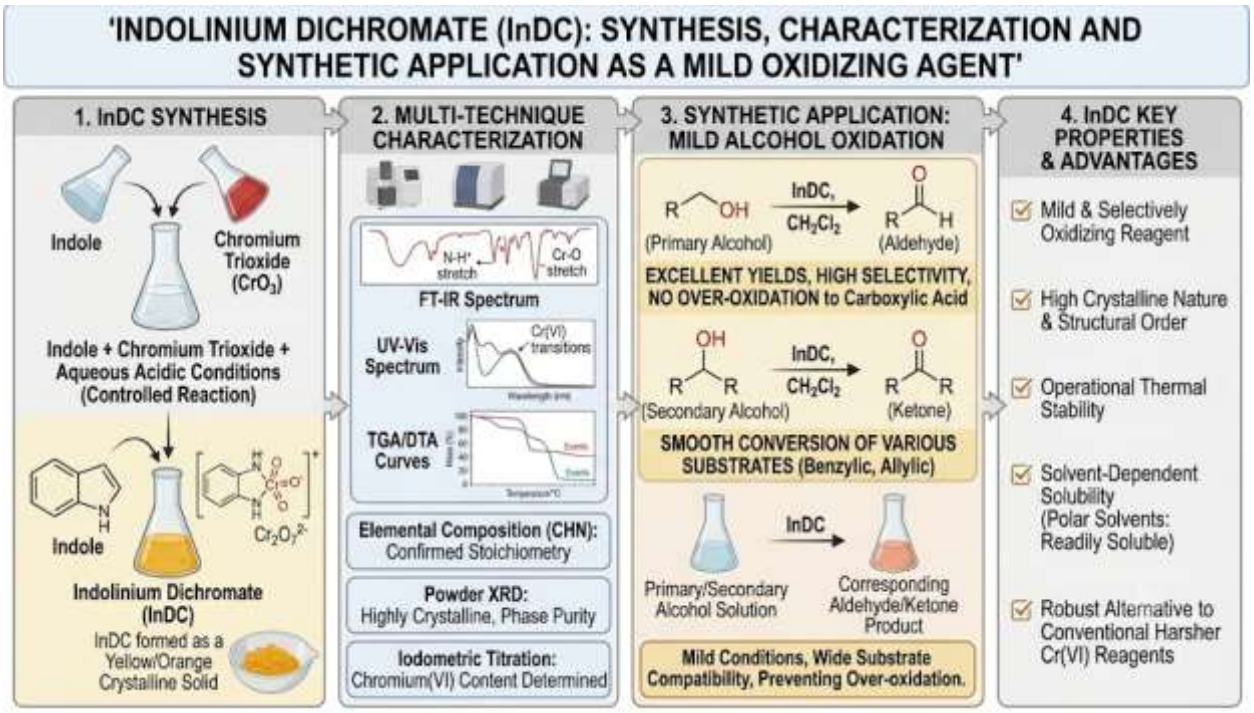
3. Benzylic alcohols to aldehydes

$3C_6H_5CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3C_6H_5CHO + 2Cr^{3+} + 7H_2O$

Benzyl alcohol is oxidized to benzaldehyde.



Graphical Abstract:



This graphical abstract illustrates the synthesis, characterization, and synthetic utility of indolinium dichromate (InDC) as a selective organic–inorganic hybrid oxidizing agent. Part I outlines the acid-catalyzed reaction between indole and chromium trioxide (CrO_3) to form InDC as a stable, yellow-orange crystalline complex consisting of protonated indolinium cations and dichromate anions. Part –II 2 highlights its comprehensive physicochemical characterization, utilizing FT-IR to confirm N-H^+ and Cr-Obond vibrations, UV-Vis for Cr(VI) electronic transitions, TGA/DTA for thermal stability, CHN elemental analysis and iodometric titration for stoichiometric purity, and Powder XRD to verify high crystallinity. Part –III demonstrates its main synthetic application in the mild oxidation of primary and secondary alcohols (including allylic and benzylic substrates) to their corresponding aldehydes and ketones without over-oxidation to carboxylic acids. Finally, Panel - IV summarizes the key advantages of InDC, emphasizing its high selectivity, operational thermal stability, excellent solubility in polar solvents, and superior safety profile relative to conventional, harsher chromium(VI) reagents.

Conclusion:

Indolinium dichromate (InDC) represents a robust, highly effective, and versatile chromium(VI)-based organic-inorganic hybrid oxidizing agent. Synthesized via the controlled reaction of indole with chromium trioxide under optimized acidic conditions, the complex successfully incorporates an organic indolinium cation to stabilize and modulate the reactive dichromate core. Comprehensive structural and physicochemical characterizations—including FT-IR, UV-Vis, ^{1}HNMR, ^{13}C NMR, elemental analysis (CHN) and Powder X-ray Diffraction (PXRD)—unanimously confirm the high purity, defined stoichiometry, and ordered crystalline nature of the complex. Spectroscopic investigations validate the distinct presence of both the protonated indolinium moiety and the dichromate ion, while thermal analysis (TGA/DTA) establishes its operational thermal stability limits and decomposition pathway.

From a synthetic perspective, InDC exhibits exceptional selectivity and efficiency as a mild oxidizing agent. It smoothly converts primary and secondary alcohols (including benzylic and allylic substrates) into their corresponding aldehydes and ketones with excellent yields under mild conditions, notably preventing unwanted over-oxidation to carboxylic acids. Its solvent-dependent solubility profile further supports its practical applicability across standard organic media. Although chromium(VI) reagents necessitate proper laboratory handling and hazardous waste management due to toxicity, indolinium dichromate stands out as a well-characterized, stable, and reliable alternative to conventional, harsher chromium oxidants in modern synthetic transformations

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