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Kinetic and Mechanistic Investigation of the Oxidation of Some α-Amino Acids by bis(2,6-dimethylpyridinium) Dichromate

Running Title: Kinetic Study of A-Amino Acid Oxidation

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Abstract: ***The kinetics and mechanism of oxidation of selected α-amino acids by bis(2,6-dimethylpyridinium) dichromate (BDMPDC) were investigated in glacial acetic acid in the presence of p-toluenesulphonic acid (TsOH). The reaction exhibits first-order dependence on BDMPDC and fractional-order dependence on both hydrogen ion and amino acid concentrations, with the latter approaching second order. Michaelis–Menten-type kinetics were observed with respect to the substrate. No significant kinetic isotope effect was detected during the oxidation of perdeuterioglycine. A small negative reaction constant obtained from correlation with Taft σ* substituent constants suggests the involvement of an electron-deficient transition state. The results indicate the formation of an intermediate complex between protonated amino acid and protonated BDMPDC, which decomposes in the rate-determining step to yield an iminium cation, followed by rapid formation of the final oxidation products.***

Keywords: kinetics; α-amino acid; oxidation; Taft σ* constants

1. Introduction

A key advancement in organic synthesis is the development of selective oxidation methods for organic substrates in non-aqueous media; accordingly, numerous Cr(VI) compounds have already been designed and synthesized.[1-5] Bis(2,6-dimethylpyridinium) dichromate (BDMPDC), composed of a 2,6-dimethylpyridinium cation and a dichromate anion [$(C_7H_{10}N)_2Cr_2O_7$], is a chromium (VI)-based oxidizing reagent. It is non-hygroscopic and insensitive to light, making it more stable and easier to store than many previously reported Cr(VI) oxidants. This reagent was first reported by Zhi-Min Jin et al.[6], in 2006. Because of its importance for both basic chemical processes and the mechanistic understanding of amino acid metabolism, the oxidation of α-amino acids is a significant field of organic chemistry. Given this significance, the present study was conducted to examine the kinetics of oxidation of a number of α-amino acids, including glycine, α-alanine, norvaline, norleucine, valine, leucine and isoleucine, by BDMPDC in glacial acetic acid medium with p-toluenesulphonic acid. The study aims to identify relationships between molecular structures and reactivity through analyzing the mechanism of oxidation of certain α-amino acids by BDMPDC.

2. Experimental

***Materials*:** BDMPDC was made using the method described[6] Melting point analysis and iodometry were used to confirm its purity. Each amino acid utilized in the investigation was of analytical reagent quality and didnot require any additional purification. We purchased perdeuterioglycine (glycine-d5: ND_2CD_2COOD) from Merck (India). After refluxing with chromium trioxide and acetic anhydride for six hours, glacial acetic acid was purified by fractional distillation. The proton source was p-toluenesulphonic acid (TsOH), whose solutions were first standardized by titrating them against a standard alkali.

Product analysis: The corresponding aldehydes were produced when the amino acids undergo oxidation. Using the described method[7], the aldehydes were transformed into their respective 2,4-dinitrophenylhydrazone (DNP) derivatives in order to conduct product analysis under kinetic circumstances. Prior to and during recrystallization, the yields of the DNP derivative for valine were 2.34 g (93%) and 2.12 g (84%), respectively. The generated DNP derivative was determined to be that of aldehyde using melting point and combined melting point measurements. Following recrystallization, similar studies using other amino acids produced the matching carbonyl compound DNP derivatives in yields ranging from 83 to 92%.

Stoichiometry: At room temperature, stoichiometric studies were performed when BDMPDC was in excess of glycine. Solutions of BDMPDC (0.015 mol) and glycine (0.003 mol) were prepared in glacial acetic acid (100 mL) containing 0.1 mol dm^{-3} TsOH. The unreacted BDMPDC was measured using spectrophotometry after the reaction mixture was let to stand for 12 h to assure completion. A stoichiometric ratio of 2:3, meaning that two moles of BDMPDC are used for every three moles of glycine, was established by a series of tests using different amounts of BDMPDC and glycine.

Kinetic measurements: A UV-Vis spectrophotometer (UV5704, ECIL) was used to examine the rate of amino acid oxidation by BDMPDC in glacial acetic acid solvent. The reduction in BDMPDC absorbance at its analytical wavelength of 364 nm was used to track the course of the reaction. By altering their concentrations in the reaction mixture, the effects of [BDMPDC] and [amino acid] on the reaction rate were investigated. Over the course of 45 minutes, kinetic measurements were performed at multiple temperatures. Absorbance values were taken every three

minutes. The observed first-order rate constants (k_{obs}) were obtained from the expression given below.

$$k_{obs} = \left(\frac{2.303}{t}\right) \log \left(\frac{(Abs)_0}{(Abs)_t}\right)$$

Here, $(Abs)_0$ and $(Abs)_t$ denote the absorbance at zero time and at time t, respectively. The reported rate constants represent the average of three independent measurements and carry an experimental error of ±4.0%. The activation parameters, namely $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$, were evaluated from temperature-dependent kinetic data. The quality of linear correlations was assessed using Exner's criterion[8] (Ψ), supplemented by the coefficient of determination (R^2 or r^2) and standard deviation (SD).

Rates and other relevant experimental data were obtained for all seven selected amino acids. As the results showed similar trends, only representative data are presented here.

Test for free radicals: Oxidation experiments performed under a nitrogen atmosphere yielded no evidence of acrylonitrile polymerization, ruling out the generation of radical intermediates. In the absence of substrate, BDMPDC concentration remained unchanged throughout the observation period. Furthermore, including acrylonitrile in the reaction mixture did not perturb the observed rate constants (Table 1), and no reduction of mercury(II) chloride[9] was detected. These control results are collectively inconsistent with a radical chain mechanism.

Table I: Observed rate constants (k_{obs}) for glycine oxidation by BDMPDC at 20 °C

[glycine] /(mol dm^{-3}	10^3[BDMPDC] /mol dm^{-3}	[H$^+$] /mol dm^{-3}	10^3 [Mn(II)] /mol dm^{-3}	$k_{obs}.10^5$ /s^{-1}
0.01	1.0	0.5	–	1.02
0.03	1.0	0.5	–	2.32
0.05	1.0	0.5	–	2.96
0.08	1.0	0.5	–	3.52
0.1	1.0	0.5	–	4.06
0.25	1.0	0.5	–	4.92
0.5	1.0	0.5	–	5.27
0.1	0.5	0.5	–	3.92
0.1	0.8	0.5	–	3.76
0.1	2.0	0.5	–	4.32
0.1	4.0	0.5	–	4.12
0.5	1.0	0.5	0.2	5.21
0.5	1.0	0.5	0.5	5.13
0.5	1.0	0.5	0.8	5.02
0.5	1.0	0.5	1.0	4.91
0.5	1.0	0.5	3.0	4.83
0.5	1.0	0.5	–	5.35*
0.5	1.0	0.5	–	5.18**

*and ** included 0.005 and 0.01 mol dm^{-3} acrylonitrile

Rate law: In the present study, the reaction shows a fractional order with respect to amino acid. The reaction is first order in BDMPDC, as the pseudo-first-order rate constant remains unchanged with variation in the oxidant (BDMPDC). A linear plot of log(absorbance) *versus* time, which stays linear up to around 80% reaction completion, lends additional support to this view. Prior to the rate-determining step, the reaction proceeds through the initial generation of an oxidant–substrate complex. The products are then produced by the breakdown of this complex (Eq. 2 and Eq. 3):

3. Result and Discussion

Amino acid is oxidized to its equivalent aldehyde as the primary product, according to stoichiometric studies and product analysis. The whole reaction can be expressed as:

$$3RCH(NH_2)COOH + 2Cr_2O_7^{2-} + 25H^+ \longrightarrow 3RCHO + 2Cr^{+3} + 3CO_2 + 3NH_4^+ + 11H_2O \quad (1)$$

$$\text{amino acid} + \text{BDMPDC} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} [\text{Complex}] \quad (2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Product} \quad (3)$$

Eq. (5) displays the rate expression that may be determined by using the steady-state approximation[13]. The predicted linear relationship between $1/k_{obs}$ and 1/ [amino acid], with a positive intercept on the rate-constant axis, is indeed observed (Fig. 1), thereby validating the proposed scheme.

$$\text{Rate} = \frac{-\,d[\text{Complex}]}{dt} = k_2\,[\text{Complex}]$$

$$\text{Rate} = \frac{K\,k_2\,[\text{amino acid}]\,[\text{BDMPDC}]_T}{1 + K\,[\text{amino acid}]} \quad (4)$$

$$\text{Rate}/\,[\text{BDMPDC}]_T = k_{obs} = \frac{K\,k_2\,[\text{amino acid}]}{1 + K\,[\text{amino acid}]} \quad (5)$$

$$(\text{Rate}/[\text{BDMPDC}]_T)^{-1} = 1/\,k_{obs} = 1/K\,k_2\,[\text{amino acid}] + 1/k_2$$

Where $K = k_1/k_{-1}$ and, and the total oxidant concentration of the oxidant is given by
$[\text{BDMPDC}]_T = [\text{Complex}] + [\text{BDMPDC}]$

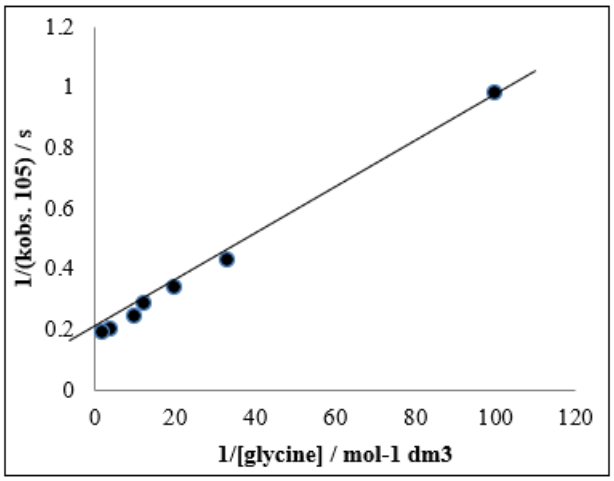


Figure 1: Plot of $1/(10^5\,k_{obs})$ vs 1/[glycine] at 20°C, [H$^+$] = 0.5 mol dm^{-3}, 10^3[BDMPDC] = 1.0 mol dm^{-3}

Temperature effect: The dependence of k_{obs} on amino acid concentration was examined over the temperature range of 20°C-50°C. Using Eq. (5), double-reciprocal plots (Fig. 1) were used to determine both the complex-formation constant (K) and the complex-decomposition constant (k_2). The

thermodynamic and activation parameters for selected amino acids were calculated (Tables 2 and 3). The activation enthalpy and entropy values indicate that rate variations are governed by contributions from both thermodynamic quantities. The relatively modest activation energy is consistent with a reaction facilitated by prior complex formation. Markedly negative $\Delta S^{\#}$ values are indicative of a highly ordered, charge-separated transition state requiring substantial solvent reorganization around the developing ionic centers.

Table II: Formation constant *(K)* and associated thermodynamic parameters for the [amino acid-BDMPDC] complexes

Substituent (R)	K / dm^{3}mol^{-1}				ΔH /kJ mol^{-1}	ΔS/mol^{-1} K^{-1}	ΔG (25°C) / kJ mol^{-1}
	20°C	30°C	40°C	50°C			
H	23.4	15.9	9.8	6.2	–37.0±1.1	–94±4	–9.8±0.9
Me	21.5	14.3	8.9	5.6	–38.0±1.0	–96±3	–9.5±0.7
Pr	19.6	12.9	7.2	4.9	–36.8±0.9	– 103±4	–9.3±1.1
Bu	22.9	14.6	8.2	5.4	–41.1±1.1	–106±3	–9.6±0.9
i-Pr	27.5	18.1	11.2	6.4	–40.6±1.7	–102±5	–10.2±1.3
i-Bu	20.8	13.2	8.3	4.6	–41.6±1.7	–109±6	–9.4±1.3
s-Bu	25.4	15.3	11.9	6.7	–35.8±2.4	–87±7	–9.9±1.8
D-gly	22.7	14.8	9.5	6	–37.3±0.7	–93±2	–9.6±0.6

Table III: Rate data (k_2) and activation parameters for the decomposition of the [amino acid- BDMPDC] complexes

Substituent (R)	$K_2 10^5$/ s^{-1}				$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/Jmol^{-1} K^{-1}	$\Delta G^{\#}$ (25°C) / kJ mol^{-1}
	20°C	30°C	40°C	50°C			
H	5.6	9.85	15.8	24.5	36.1±0.5	–203±2	96.6±0.4
Me	12.7	21.2	31.2	42.6	29.2±1.3	–220±4	94.6±0.9
Pr	15.7	24.9	32.2	48.3	26.1±1.3	–229±3	94.2±1.0
Bu	16.1	25.3	35.9	49.2	25.3±1.4	–231±5	94.2±1.0
i-Pr	17.8	27.5	39.4	52.8	26.2±0.5	–228±3	93.8±0.6
i-Bu	15.9	25.2	35.7	48.9	26.8±0.8	–226±2	94.1±0.7
s-Bu	18.1	28.4	40.5	53.6	25.9±1.1	–228±3	93.8±0.8
D-gly	5.9	9.21	16.9	21.8	33.2±2.1	–213±7	96.5±1.8
k_H/k_D	0.95	1.07	0.93	1.12			

Effect of TsOH concentration: A systematic increase in the concentration of TsOH, the source of hydrogen ions, leads to a progressive increase in the reaction rate. A logarithmic plot of k_{obs} against [H$^+$] for glycine yields a line (r^2= 0.9916) with slope ~1.32 signifying a fractional order (<2) for TsOH, consistent with a pre-equilibrium protonation mechanism (Table 4). Plotting $1/k_{obs}$ against $1/[H^+]^2$ gives a straight line with a finite positive intercept (Fig. 2), leading to the empirical expression:

$$1/k_{obs} = 1/k_o + a/[H^+]^2 \quad (6)$$

In Eq. (6), k_o designates the rate constant for the uncatalyzed pathway and 'a' represents the slope of the linear fit. Qualitatively similar acid-dependent rate profiles have been documented for the oxidation of alcohols and related substrates by various Cr(VI) reagents, including ethylenediammonium dichromate.[10]

Table IV: Dependence of the reaction rate on hydrogen-ion concentration [glycine] = 0.5 mol dm^{-3}; 10^3[BDMPDC] = 1.0 mol dm^{-3}; temperature 20°C

[TsOH] / mol dm^{-3}	0.05	0.1	0.2	0.3	0.5	0.75
$10^5 k_{obs}$/s^{-1}	0.24	0.56	1.89	3.15	5.27	3.85

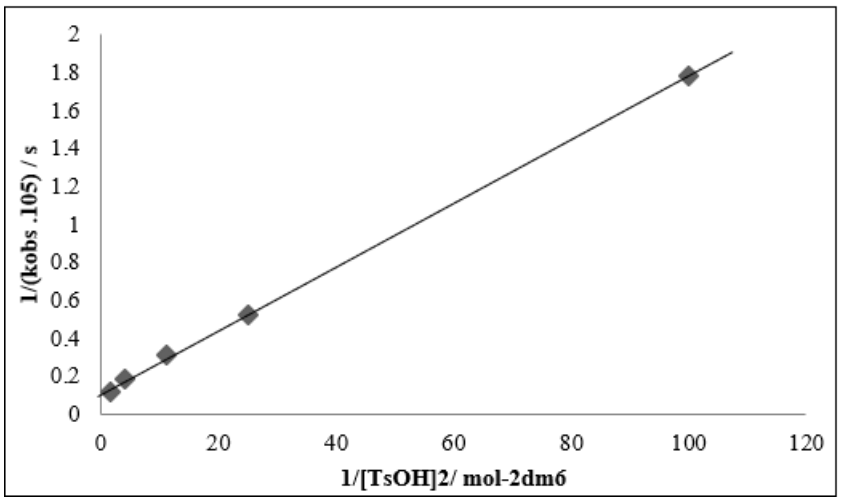


Figure 2: Plot of $1/(10^7 k_{obs})$ vs $1/[TsOH]^2$ at 20°C, [glycine] = 0.5 mol dm^{-3}, 10^3[BDMPDC] = 1.0 mol dm^{-3}

Kinetic isotope effect: The oxidation of perdeuterioglycine (glycine-d5) was examined to ascertain the importance of α-C–H bond breaking in the rate-determining stage. With a k_H/k_D ratio of 0.95 at 20°C, the results, which are summarized in Table 3, showed no discernible kinetic isotope impact.

Mn(II) ion influence: The impact of additional Mn(II) ions on the reaction mixture was investigated in order to enquire to the potential role of Cr(IV) as an intermediate during the reaction. Table 1 provides a summary of the experimental findings.

Isokinetic relationship: For the seven amino acids, the Exner's plot of log k_2 values at 20°C and 50°C shows a strong linearity (slope = 0.664 ± 0.006; r^2 = 0.9996). Using the Exner approach, the isokinetic temperature was determined to be 405±2K. The validity of linear free-energy connections depends on the observed linear isokinetic relationship.[11] Additionally, it implies that a same mechanism underlies all correlated reactions.

Mechanistic evidence for Cr(IV) intermediate formation: Two potential electron-transfer pathways have been suggested[12] for the oxidation processes of chromium (VI) complexes. In contrast to the second, which progresses by a coordinated two-electron transfer in a single step, the first includes repeated one-electron transfer stages. As a result, either Cr(V) or Cr(IV) intermediate species may be formed throughout the reactions.[13,14,15] The likelihood of a Cr(V) intermediate in the current oxidation of amino acids by BDMPDC is ruled out by the negative test for free-radical production.

The observed reduction in the oxidation rate following the addition of Mn(II) ions to the reaction mixture supports the participation of a Cr(IV) intermediate during the process. Since the redox potential of the Mn(III)/Mn(II) pair is 1.51 V while that of the Cr(VI)/Cr(III) couple is 1.33V[16], Mn(II) is widely acknowledged as an effective scavenger for Cr(IV) intermediates. This suggests that it is thermodynamically adverse for Cr(VI) to directly oxidize Mn(II). As shown by the following equation, if a Cr(IV) intermediate is created during the reaction, the additional Mn(II) ions can successfully trap it, removing it from the reaction pathway and lowering the oxidation rate:

$$Mn(II) + Cr(IV) = Mn(III) + Cr(III)$$

Strong evidence that a Cr(IV) intermediate is involved in the reaction process is provided by the observed drop in the oxidation rate following the addition of Mn(II) ions[17] (Table 2). The state of BDMPDC under our reaction conditions is non-ionic in nature. Thus, it does not dissociate as dichromate and 2,6-dimethylpyridinium ions. A combination of the zwitterionic (**a**) and mostly protonated, or cationic (**b**) forms of amino acids can be found in acidic media:

$$\underset{\textbf{(a)}}{RCH(N^+H_3)COO^-} + H^+ \overset{K_a}{\rightleftharpoons} \underset{\textbf{(b)}}{RCH(N^+H_3)COOH} \quad (7)$$

The species **d,** is produced when BDMPDC **(c)** is protonated in the presence of hydrogen ions. In the reactions of BDMPDC and other heterocyclic Cr(VI) oxidants[18], where the protonated form functions as a stronger oxidizing species, the development of such protonated Cr(VI) species has previously been suggested.

$$\underset{\textbf{(c)}}{(DMPH)_2Cr_2O_7} + H^+ \overset{K_b}{\rightleftharpoons} \underset{\textbf{(d)}}{(OH)OCr^+(OCrO_2O^-DMPH^+)\,(O^-DMPH^+)} \quad (8)$$

Where DMP denotes dimethylpyridine

Correlation study of oxidation reactivity: According to the following connection, the amino acid oxidation rates showed a strong link with the Taft σ* substituent constants, resulting in low negative reaction constants (Table 6):

$$\log k_2 = \rho^* \sigma^* + \log k_o \quad (9)$$

The documents published by Wiberg[19] were the source of the substituent constant values. The polar reaction constant's small negative value suggests that while electron-withdrawing groups slow down the oxidation process, electron-donating groups a little increase the reaction rate.

Table V: Temperature dependence of the reaction constant (ρ*)

Temperature (°C)	ρ*	r^2	SD	Ψ	n
20	–0.72±0.01	0.999	0.005	0.03	7
30	–0.65±0.01	0.9995	0.003	0.02	7
40	–0.56±0.02	0.9869	0.007	0.12	7
50	–0.48±0.03	0.9997	0.002	0.018	7

'n' is the number of experimental data points.

Mechanism: Several lines of evidence preclude a single-electron radical mechanism: (i) acrylonitrile, a sensitive radical trap, caused no acceleration of polymerization when added to the reaction mixture; (ii) mercury (II) chloride remained unreacted throughout, confirming that one-electron oxidation are not formed in the primary step. The lack of a substantial kinetic isotope have an effect suggests that the rate-determining step does not include breakage of the α-C–H bond. The polar reaction constant's negative value indicates that substituents that release electrons speed up the reaction. This might be explained by a higher electron density in the direction of the carboxyl group, which makes it easier for an intermediate complex to form and speeds up the oxidation process. The reaction center is comparatively far from the site of substitution, as further evidenced by the low magnitude of the reaction constant. The formation of a 1:1 intermediate complex through a quick pre-equilibrium step involving nucleophilic attack by the hydroxyl oxygen of the cationic form of the amino acid on the protonated oxidant species, $BDMPDCH^+$, is supported by the observed Michaelis–Menten-type kinetics with respect to the amino acid concentration. The resultant complex then proceeds through a quick phase that results in the development of an iminium

cation after undergoing decomposition in the rate-control stage. Cr(VI) is reduced to a Cr(IV) species during this process (Scheme 1).

According to the suggested mechanism:

$$\text{Rate} = -\,d[\text{BDMPDC})]/dt = k_2\,[\mathbf{e}] \qquad (10)$$

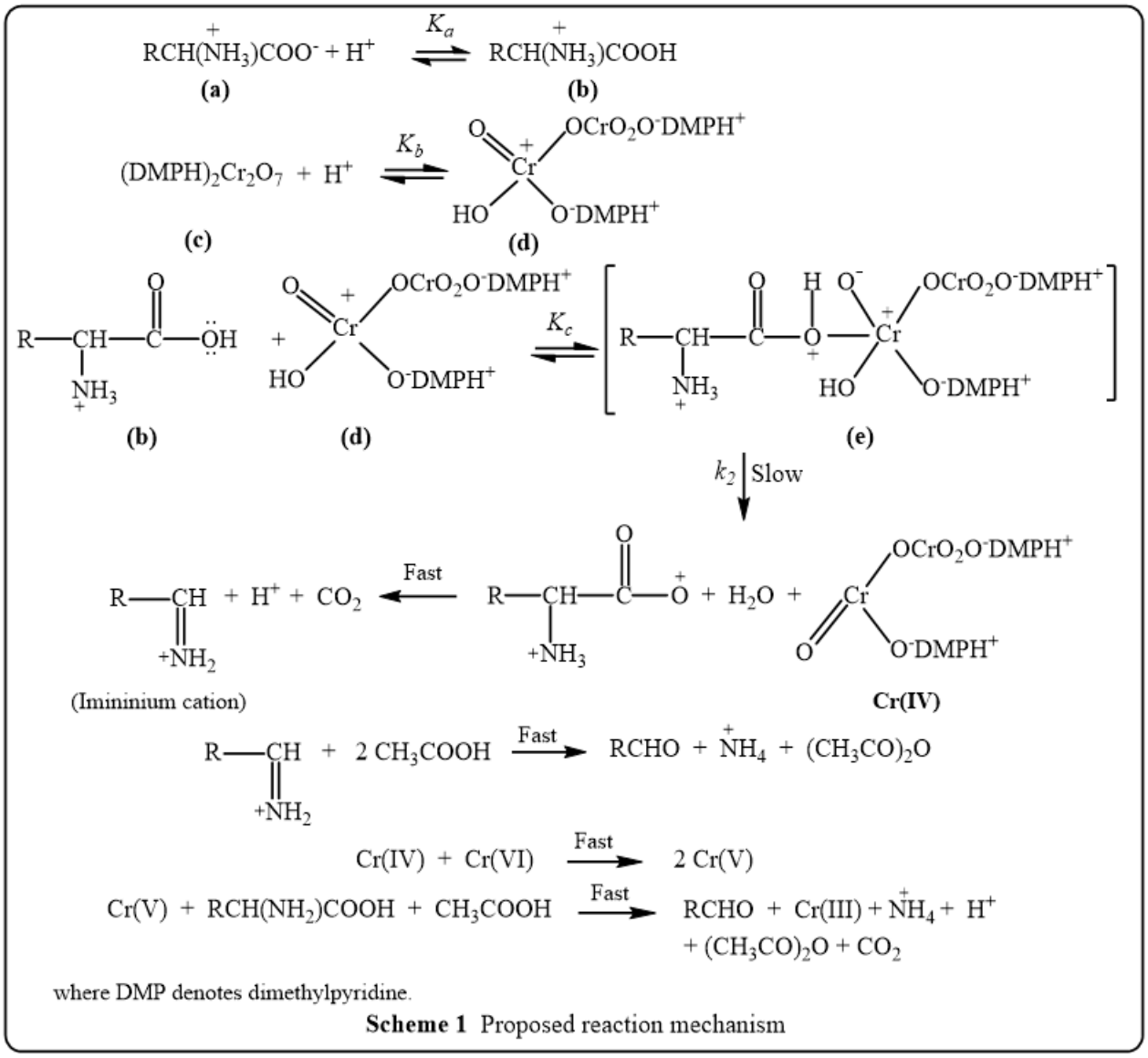
Also, K_a = [protonated amino acid] / [H^+] [amino acid] (11)

K_b = [$BDMPDCH^+$] / [H^+] [BDMPDC] (12)

K_c = [**e**] / (protonated amino acid] [$BDMPDCH^+$]) (13)

Combining equations (10) to (13), we get:

$$\text{rate} = k_2\ K_aK_bK_c\ [\text{amino acid}]\ [H^+]^2\ [\text{BDMPDC}] \qquad (14)$$



Scheme 1 Proposed reaction mechanism

The total concentration of BDMPDC may be expressed as $[\text{BDMPDC}]_t$ = [BDMPDC] + [e]. It is assumed that the protonated species, $BDMPDCH^+$, is rapidly consumed in the formation of the intermediate complex 'e' immediately after its generation. Using Eq. (14):

$$[\text{BDMPDC}] = [\text{BDMPDC}]_T/(1 + K_aK_bK_c\,[H^+]^2[\text{amino acid}]) \qquad (15)$$

Similarly, the total concentration of the amino acid can be represented as $[\text{amino acid}]_t$ = [amino acid] + **[e]**. The protonated amino acid species **(d)** is assumed to be rapidly consumed in the formation of the intermediate complex '**e**' immediately after its formation. Using Eq. (14):

$$[\text{amino acid}] = [\text{amino acid}]_T/(1+ K_aK_bK_c\,[H^+]^2[\text{BDMPDC}]) \qquad (16)$$

Considering the low concentration of BDMPDC employed, the term $K_aK_bK_c$ [BDMPDC] $[H^+]^2$ in the above equation may be neglected. Consequently, the free amino acid concentration becomes approximately equal to the total amino acid concentration, i.e.,

$$[\text{amino acid}] = [\text{amino acid}]_T \qquad (17)$$

In view of the relatively high concentration of hydrogen ions, the free hydrogen ion concentration may be considered equal to its total concentration. Combining Eqs. (14) to (17), the following expression is obtained:

$$\text{rate} = \frac{k_2\,K_a\,K_b\,K_c\,[\text{amino acid}]\,[H^+]^2}{1 + K_a\,K_b\,K_c\,[\text{amino acid}]\,[H^+]^2}$$

$$\text{Or, rate}/[\text{BDMPDC}]_T = k_{obs} = \frac{k_2 K_a K_b K_c [\text{amino acid}] [H^+]^2 [\text{BDMPDC}]_T}{K_a K_b K_c [\text{amino acid}] [H^+]^2} \quad (19)$$

The following form (20), which is appropriate for verification, can be created by rearranging the rate law (19):

$$1/k_{obs} = 1/ k_2 K_a K_b K_c [\text{amino acid}] [H^+]^2 + 1/k_2 \quad (20)$$

Eq. (19) satisfactorily accounts for the experimentally observed kinetic orders with respect to the various reacting species. Comparison of Eq. (5) and (20) yields the relation:

$K = K_a K_b K_c [H^+]^2$

Equation (20) states that, as shown experimentally, a plot of $1/k_{obs}$ versus 1/[amino acid] at constant $[H^+]$ should be a straight line with a positive intercept on the $1/ k_{obs}$ axis. Additionally, a plot of $1/ k_{obs}$ *versus* $1/[H^+]^2$ at constant [amino acid] is likewise a straight line with a positive intercept on the $1/k_{obs}$ axis, supporting the viability of the suggested mechanism.

First, Cr(VI) is reduced to Cr(IV), which then combines up with another species of Cr(VI) to form Cr(V). The Cr(V) intermediate is then rapidly reduced to the end product, Cr(III). A number of redox alterations are known to occur during Cr(VI)-mediated oxidations[16].

4. Conclusion

The oxidation of all selected α-amino acids by bis(2,6-dimethylpyridinium) dichromate (BDMPDC) in glacial acetic acid medium is first order with respect to BDMPDC and fractional order with respect to amino acids and hydrogen-ion concentrations. The reaction proceeds through the formation of an intermediate amino acid–BDMPDC complex, followed by its rate-determining decomposition. The absence of a significant kinetic isotope effect and free-radical involvement, together with Mn(II) inhibition studies, supports a mechanism involving a Cr(IV) intermediate. The observed substituent effects and activation parameters are consistent with a common mechanism for all the amino acids investigated. The proposed rate law satisfactorily explains the experimental kinetic results.

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