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Oxidative cleavage of lysine by nicotinium dichromate in aqueous medium in presence of perchloric acid

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ABSTRACT

The oxidation of an essential amino acid like lysine by nicotinium dichromate in aqueous medium in the presence of perchloric acid was studied. The reaction was first order with respect to oxidant, fractional order with respect to substrate and second order with respect to perchloric acid. The increase in ionic strength had negligible effect on the rate. Amino acid was converted to the corresponding carbonyl compound. No polymerisation was observed with acrylonitrile. The addition of Mn^{2+} ion had a noticeable catalytic effect on the rate. The rates were determined at four different temperatures and the thermodynamic parameters were evaluated.

Keywords: kinetics, oxidation, lysine, nicotinium dichromate, mechanism.

INTRODUCTION

Nicotinium dichromate (NDC) is a stable, non-hygroscopic, mild and selective oxidant in synthetic organic chemistry [1]. A review of literature shows that kinetic studies using this reagent are meager [2-13]. There is no significant data on the oxidation of lysine by NDC. Hence the kinetics of oxidation of lysine by NDC has been studied in aqueous medium in the presence of perchloric acid.

MATERIALS AND METHODS

Materials

Chromatographically pure amino acid - lysine (LOBA) was used. Perchloric acid (AnalaR) was used as a source of hydrogen ions. All other reagents used were of analytical grade. Doubly distilled water was used throughout the study.

Preparation of Nicotinium dichromate

Nicotinium dichromate (NDC) was prepared by the reported method [1] and its purity was checked by iodometric estimation of the amount of Cr (VI) present in it and the aqueous stock solution of NDC was prepared, standardized and preserved in dark coloured bottles.

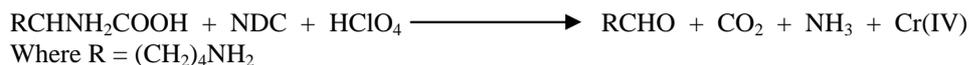
Kinetic measurements

The reactions were carried out under pseudo-first order conditions by maintaining a large excess of the amino acid over NDC. The reactions were followed at constant temperature (313 K). Kinetic studies have been carried out by colorimetric method using photoelectric colorimeter with 470 nm. The rate constants were evaluated from the linear plot of $\log(\text{absorbance})$ versus time by the least square method and were reproducible within $\pm 3\%$.

Product analysis and Stoichiometry

The main products of the oxidation of amino acids were the corresponding aldehydes, ammonia and carbon dioxide. The presence of ammonium ions in the reaction mixture was detected by the test with *p*-nitrobenzenediazoniumchloride [14]. The presence of carbon dioxide in the product was identified by lime water test [15]. The aldehyde was determined as its 2, 4-dinitrophenylhydrazone (DNP). In a typical experiment, amino acid (0.05 M) and NDC (0.01 M) were made up to 100 ml in 0.5 M perchloric acid. The reaction mixture was allowed to stand for 12 h in the dark to ensure the completion of the reaction. Then it was treated with an excess (250 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 M HCl and kept in a refrigerator for 10 h. The precipitated DNP was filtered off, dried, weighed, recrystallised from ethanol and weighed again. The yield was 85%. The DNP was found to be identical (mp and mixed mp) with the DNP of the corresponding aldehyde.

The stoichiometric analysis showed that one mole of amino acid was consumed by one mole of the oxidant.



RESULTS AND DISCUSSION

Effect of NDC

The [NDC] was varied in the range 6.0×10^{-3} to 14.0×10^{-3} mol dm⁻³ at constant [lysine], [H⁺] at 313 K and the rates were measured. The near constancy in the value of *k*_{obs} irrespective of the concentration confirms the first order dependence on NDC (Table 1) [16].

Effect of lysine

The [lysine] was varied in the range from 2.0×10^{-2} to 6.0×10^{-2} mol dm⁻³ at 313 K and keeping all other reactant concentrations constant and the rates were measured. The rate constant increased with increase of [lysine] (Table 1). The order of the reaction with respect to [lysine] was found to be fractional as evidenced by the slope (0.54) of the plot of log *k*_{obs} versus log [lysine]. A plot of 1/ *k*_{obs} versus 1/ [lysine] shows an intercept on the rate axis, indicating the Michaelis - Menten dependence on lysine [17, 18].

Effect of perchloric acid

The [perchloric acid] was varied within the range 5.0×10^{-2} to 15.0×10^{-2} mol dm⁻³ at 313 K and keeping all other reactant concentrations constant and the rates were measured. The rate constant increased with increase of [perchloric acid] (Table 1). The plot of log *k*_{obs} versus log [H⁺] gave a straight line with a slope (2.23). It has been observed that the order in [perchloric acid] is two.

Table - 1 Rate constants for the oxidation of lysine by NDC at 313 K in aqueous medium in the presence of perchloric acid

[NDC] × 10 ³ (mol dm ⁻³)	[lysine] × 10 ² (mol dm ⁻³)	[H ⁺] × 10 ² (mol dm ⁻³)	<i>k</i> _{obs} × 10 ⁴ (s ⁻¹)
6.0	2.0	5.0	3.21
8.0	2.0	5.0	3.28
10.0	2.0	5.0	3.20
12.0	2.0	5.0	3.29
14.0	2.0	5.0	3.25
6.0	2.0	5.0	3.21
6.0	3.0	5.0	4.07
6.0	4.0	5.0	4.71
6.0	5.0	5.0	5.32
6.0	6.0	5.0	5.84
6.0	2.0	5.0	3.21
6.0	2.0	7.5	9.12
6.0	2.0	10.0	16.59
6.0	2.0	12.5	26.58
6.0	2.0	15.0	37.47

Effect of ionic strength

The change in ionic strength by the addition of sodium perchlorate has no effect on the rate (Table 2). This shows that the reaction may be between an ion and a neutral molecule or between neutral molecules [19].

Effect of MnSO₄

The rate decreases with increasing the [Mn²⁺] ion confirming the involvement of two electron transfer process in this reaction (Table 2) [20].

Table – 2 Effect of NaClO₄ and MnSO₄ on the oxidation of lysine by NDC

[NaClO ₄] × 10 ³ (mol dm ⁻³)	[MnSO ₄] × 10 ³ (mol dm ⁻³)	k _{obs} × 10 ⁴ (s ⁻¹)
0.0	0.0	3.21
1.0	0.0	3.19
2.0	0.0	3.21
3.0	0.0	3.23
4.0	0.0	3.20
0.0	0.0	3.21
0.0	1.0	3.13
0.0	2.0	2.93
0.0	3.0	2.84
0.0	4.0	2.79

$$[\text{lysine}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}; [\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}; [\text{NDC}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Test for free radicals

No polymerisation is observed with acrylonitrile. The reaction mixture when allowed to stand with acrylonitrile does not induce polymerisation suggesting the absence of free radical mechanism.

Effect of temperature

The rate of the oxidation of amino acid was determined at different temperatures (303–333K) and the activation parameters were evaluated (Table 3).

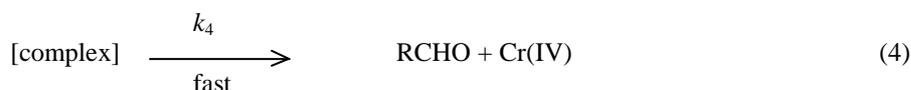
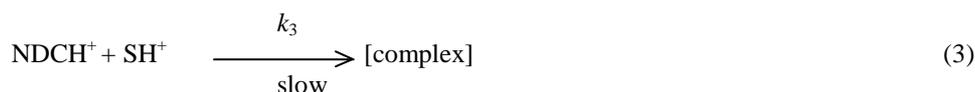
Table - 3 Thermodynamic and activation parameters for the oxidation of amino acids by NDC

Substrate	k _{obs} × 10 ⁴ (s ⁻¹)				ΔH [#] (kJ mol ⁻¹)	ΔS [#] (J K ⁻¹ mol ⁻¹)	ΔG [#] (kJ mol ⁻¹)	E _a (kJ mol ⁻¹)
	303 K	313 K	323 K	333 K				
Lysine	1.44	3.21	5.99	11.65	55.39	-103.40	87.75	57.99

$$[\text{lysine}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}; [\text{NDC}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}; [\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$$

Mechanism and rate law

It is clear that the reaction has first order with respect to NDC, fractional order with respect to lysine and second order with respect to H⁺. The ionic strength of the medium has a negligible effect on the rate, the added Mn²⁺ had a catalytic effect on the reaction rate and the absence of free radicals during the course of the reaction. The observed data can be explained on the basis of the following mechanism.



The above mechanism leads to the following rate law:

$$\text{rate} = k_3 [\text{Complex}]$$

$$= \frac{K_2 k_3 [\text{SH}^+] [\text{H}^+]}{1 + K_2 [\text{S}]} \quad (5)$$

$$= \frac{K_1 K_2 k_3 [\text{NDC}] [\text{S}] [\text{H}^+]^2}{1 + K_2 [\text{S}]} \quad (6)$$

Equation (6) accounts for first order dependence on [NDC], second order dependence on [HClO₄] and fractional order dependence on [lysine]. Equation (4) indicates the involvement of a two-electrons reduction of Cr(VI) to Cr(IV) which is confirmed by the decrease in the rate constant with the addition of MnSO₄ (Table 2).

CONCLUSION

The oxidation of lysine by NDC in aqueous medium in the presence of perchloric acid leads to the formation of a complex giving corresponding aldehyde as the final product. The reaction follows pseudo-first order kinetics. Increase in temperature increases the rate of the reaction. The activation parameters are evaluated from the study of oxidation at different temperatures. The mechanism proposed for this oxidation kinetics is in accordance with the observed kinetic facts. The negative sign of the entropy change suggests that the transition state is more orderly when compared with the reactants.

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