

KINETICS AND MECHANISM OF 4, 5 - DIAZOPHENANTHRENE [4,5-DIAZOPHEN] CATALYZED OXIDATION OF 2-AMINO-4- (METHYLTHIO)BUTANOIC ACID BY QUINALDINIUM FLUOROCHROMATE [QNFC] IN AQUEOUS ACETIC ACID MEDIUM

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ABSTRACT

Kinetics of oxidation of [2-amino-4-(methylthio)-butanoic acid] by [QNFC] in protic solvent system has been studied at 308 K. The product has been identified as corresponding ketonic group. A first order dependence of the reaction with respect to [QNFC] [2-amino-4-(methylthio)-butanoic acid] and the fractional order [H⁺] has been observed. The rate constant increased with increase in the concentration of perchloric acid. The reaction has been found to be catalyzed by H⁺ ions. Increasing the percentage of the acetic acid medium increases the rate. Addition of sodium perchlorate increases the rate of reaction appreciably. No polymerization with acrylonitrile. The reaction has been conducted at four different temperature and the activation parameters were calculated. From the observed kinetic results a suitable mechanism was proposed.

Keywords : kinetics, oxidation, 2-amino-4-(methylthio)-butanoic acid , QNFC, 4,5-diazophenanthrene

1, INTRODUCTION

Oxidation reaction has been a subject of major importance to many chemists and elucidation of the mechanism is undoubtedly one of the most fascinating problems in the mind of chemists. The investigation of reaction kinetics in chemical reactions is the most important in deciding the reaction mechanisms. The kinetics deal with the study of change in concentrations of the components of the reaction system with the passage of time and the results are summarized in the form of rate expressions.

1.1 Quinaldinium fluorochromate (VI) as an oxidant:

Chromium compounds have been widely used in aqueous and non-aqueous media for the oxidation of a variety of organic compounds [1-5]. Chromium compounds have been proved to be versatile reagents for the oxidation of almost all the organic functional groups [6-9]. Generally chromium(VI) oxidation reactions have been performed in aqueous acidic conditions, the source of chromium(VI) being chromium trioxide, sodium dichromate, potassium dichromate, chromyl chloride, chromyl acetate, t-butyl chromate (or) co-oxidation complexes of chromium trioxide. However, a variety of new chromium(VI) oxidants along with special reagents have been introduced for the chemospecific, regiospecific and stereospecific oxidation of functional groups in highly sensitive systems [10-16].

Polymer supported chromium(VI) reagents have also been developed. These reagents offer the advantage of simplifying the work procedure. Recently, some neutral chromium(VI) reagents like benzimidazolium fluorochromate (BIFC), pyridinium fluorochromate (PFC), nicotinium dichromate (NDC) etc., have been developed to effect of oxidation under mild conditions. The oxidant quinaldinium fluorochromate (QNFC) [17-22] is used in the present work. The complexing agents like 4,5-diazophenanthrene (4,5-diazophen) are used in the present investigation for the oxidation process as a catalyst.

1.2 Oxidation of [2-amino-4-(methylthio)butanoic acid]:

Oxidation reaction the most important role of kinetic reaction, like to the 2-amino-4-(methylthio)-butanoic acid oxidations.

2. MATERIALS AND METHODS

2.1 Preparation of [2-amino-4-(methylthio)butanoic acid]:

The corresponding 2-amino-4-(methylthio)-butanoic acid was prepared as described by Krishnasamy *et al.*

2.2 Other chemicals:

[QNFC] was prepared by the method described in the literature [23]. All other chemicals were used as supplied without further purification used in this experiment are all of AR grade samples.

2.3 Product analysis and stoichiometry oxidation of [2-amino-4-(methylthio)butanoic acid] by [QNFC]:

Product analysis was carried out by taking the reaction mixture containing 2-amino-4-(methylthio)butanoic acid (0.01 mol), HClO₄ (2 M), QNFC (0.01 mol) was dissolved in aqueous acetic acid (20 mL) and allowing it to stand for 2 h at 50 °C. Thereafter 10 mL of sodium bicarbonate was added and the solution stirred vigorously, followed by drop wise addition of benzoyl chloride solution with precipitation was completed. The precipitate was identified as N-benzoyl-2-amino-4-(methylthio)butanoic acid sulfoxide (m.p. 183 °C) as a derivative of 2-amino-4-(methylthio)butanoic acid sulfoxide. The IR spectrum showed that the new band for >S=O is appeared at 1050-1110 cm⁻¹ for the product. The estimation of unreacted QNFC indicated that 1 mol of substrate consumed 1 mol of QNFC.

2.4 Purification of water:

Deionized water was distilled twice in a corning vessel. The second distillation was over potassium permanganate. All solutions were prepared from double distilled water. The following solutions of required concentrations were prepared and used for the kinetic studies: i) QNFC, perchloric acid, sodium perchlorate and manganous sulfate in water, ii) 2-amino-4-(methylthio)butanoic acid in acetic acid.

2.5 Kinetics and oxidation of [2-amino-4-(methylthio)butanoic acid] by [QNFC]:

All the kinetic reactions were carried out under pseudo-first order conditions, keeping [substrate] >> [QNFC] in a solvent system of 50% (v/v) acetic acid-water medium at 308 K unless otherwise mentioned and the course of the reaction were followed by iodometrically.

3. RESULTS AND DISCUSSION

3.1. Effect of varying [QNFC]

The reactions were conducted with varying concentrations of QNFC and keeping all other reactant concentrations constant and the rate constants were calculated (Table.1). In both the 4,5-diazophenanthrene catalyzed reactions. First order dependence on QNFC was evidenced from the linear plots of log titre *versus* time.

Table 1. Effect of varying [QNFC] concentration

[2-Amino-4-(methylthio)-
butanoic acid] = $10.00 \times 10^{-3} \text{ mol dm}^{-3}$,
[4,5-Diazophen] = $15.0 \times 10^{-3} \text{ mol dm}^{-3}$
[HClO₄] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$
Solvent = 50-50 (% v/v) AcOH-H₂O
Temperature = 308 K

10^3 [QNFC] (mol dm^{-3})	10^3 [QNFC] (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
0.75	0.75	4.67
1.00	1.00	5.75
1.25	1.25	5.94
1.50	1.50	6.09
1.75	1.75	6.85
2.00	2.00	7.22

3.2. Effect of varying [2-amino-4-(methylthio)butanoic acid]

The reactions were investigated with varying concentration of 2-amino-4-(methylthio)butanoic acid and keeping all other reactant concentrations constant and the observed rate constant values were given in Table .2. A plot of $\log k_{\text{obs}}$ versus \log [2-amino-4-(methylthio)butanoic acid] is linear with a slope = 1.02, $r = 0.991$, $sd = 0.021$ in the case of 4,5-diazophenanthrene catalyzed reaction. These results show that first order dependence with respect to [2-amino-4-(methylthio)butanoic acid] in the case of 4,5-diazophenanthrene catalyzed reaction.

Table 2. Effect of varying [2-amino-4-(methylthio)butanoic acid] concentration

[QNFC] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$
[4,5-Diazophen] = $15.0 \times 10^{-3} \text{ mol dm}^{-3}$
[HClO₄] = $5.00 \times 10^{-3} \text{ mol dm}^{-3}$
Solvent = 50-50 (% v/v) AcOH-H₂O
Temperature = 308 K

$10^4 k_{\text{ob}}$ (s^{-1})	10^3 [2-Amino-4-(methylthio)- butanoic acid] (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
1.93	05.00	3.40
2.67	07.50	4.13
3.43	10.00	5.75
3.96	12.50	6.42
4.67	15.00	6.74
4.96	17.50	7.07
5.46	20.00	8.55
6.09	22.05	9.26
6.85	25.00	11.30

3.3. Effect of varying [HClO₄]

The reactions were carried out with varying concentration of perchloric acid and keeping all other reactant concentrations constant. The rate constants increased with increase in the concentration of perchloric acid (Table. 3). The plot of $\log k_{\text{obs}}$ versus $\log [H^+]$ shows that fractional order dependence is observed (slope = 0.346; r = 0.995; sd = 0.014) in the case of 4,5-diazophenanthrene catalyzed reaction.

Table . 3. Effect of varying [HClO₄] concentration

[2-Amino-4-(methylthio)-
butanoic acid] = $10.0 \times 10^{-3} \text{ mol dm}^{-3}$
[QNFC] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$
[4,5-Diazophen] = $15.0 \times 10^{-3} \text{ mol dm}^{-3}$
Solvent = 50-50 (% v/v) AcOH-H₂O
Temperature = 308 K

$10^3 [\text{HClO}_4]$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
02.5	4.26
05.0	5.75
10.0	6.01
15.0	7.54
20.0	8.89
25.0	9.79

3.4. Effect of varying [4,5-diazophenanthrene]

The 4,5-diazophenanthrene catalyzed reaction was carried out with varying concentration of 4,5-diazophenanthrene and keeping all other reactant concentrations constant and measured the rate constant values were given in Table.4 The rate constant increased with increasing the concentration of 4,5-diazophenanthrene. The plot of $\log k_{\text{obs}}$ versus $\log [4,5\text{-diazophen}]$ is a straight line with a slope = 0.86, r = 0.997; sd = 0.017 (Fig.1) shows that first order dependence with respect to [4,5-diazophen].

Table .4. Effect of varying [4,5-diazophenanthrene] concentration

[2-Amino-4-(methylthio)-
butanoic acid] = $10.0 \times 10^{-3} \text{ mol dm}^{-3}$
[HClO₄] = $5.00 \times 10^{-3} \text{ mol dm}^{-3}$
[QNFC] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$
Solvent = 50-50 (% v/v) AcOH-H₂O
Temperature = 308 K

$10^3 [4,5\text{-diazophen}]$ (mol dm^{-3})	$10^4 k_{\text{obs}}$ (s^{-1})
05.00	2.37
10.00	3.34
15.00	5.75
20.00	6.97
25.00	7.43
30.00	9.27

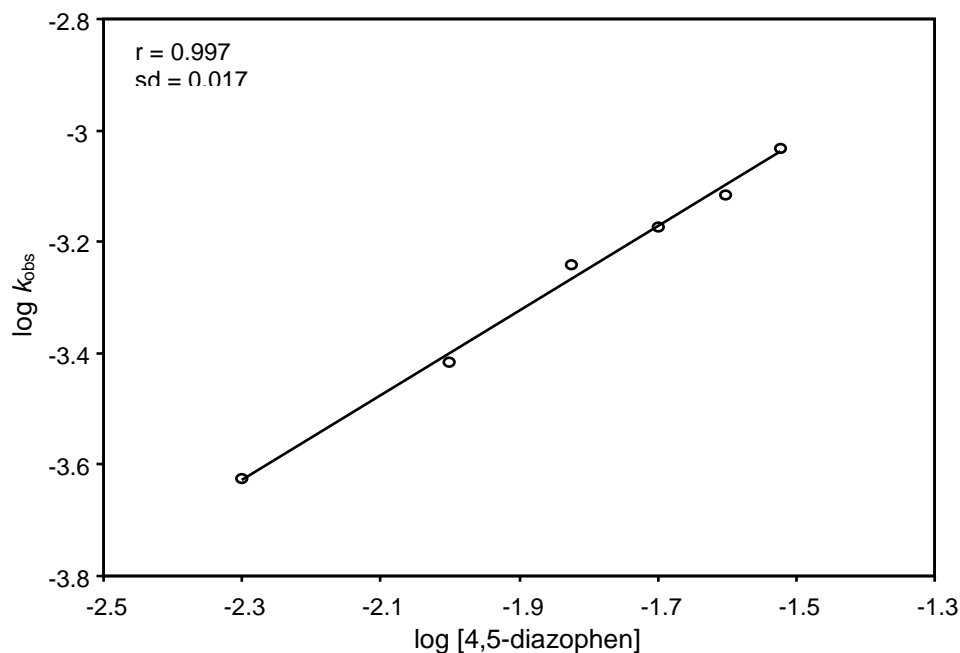


Fig..1. Plot of log k_{obs} versus log [4,5-diazophenanthrene]

3.5. Effect of varying solvent composition

Both the uncatalyzed and 4,5-diazophenanthrene catalyzed reactions were conducted with different solvent composition of acetic acid-water mixture and keeping all other reactant concentrations constant and the corresponding rate constants were given in Table .5. 4,5-diazophenanthrene catalyzed reactions. This suggests that an ion-dipole interaction may be involved in the mechanistic pathway. A plot of log k_{obs} versus $1/D$ is linear with a positive slope in 4,5-diazophenanthrene catalyzed reactions.

Table .5. Effect of varying solvent composition

[2-Amino-4-(methylthio)-

butanoic acid] = $10.0 \times 10^{-3} \text{ mol dm}^{-3}$ [QNFC] = $1.0 \times 10^{-3} \text{ mol dm}^{-3}$

[HClO₄] = $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ [4,5-Diazophen] = $15.0 \times 10^{-3} \text{ mol dm}^{-3}$

Temperature = 308 K

AcOH-H ₂ O (% v/v)	$10^4 k_{ob} (s^{-1})$
30-70	1.87
35-65	2.61
40-60	3.67
45-55	4.13
50-50	5.75
55-45	6.86
60-40	7.22
65-35	8.89
70-30	9.31

3.6. Effect of added [NaClO₄], [acrylonitrile] and [MnSO₄]

The rate data was measured with different concentration of NaClO₄ and keeping all other reactant concentrations constant. The rate constants slightly decrease with increase in the concentration of NaClO₄ suggest that the reaction may be between an ion and a neutral molecule. Added acrylonitrile rules out the possibility of radical pathway mechanism. Added Mn²⁺ showing catalytic effect on the reaction rate in 4,5-diazophenanthrene catalyzed reactions (Table .6).

Table 6. Effect of varying [NaClO₄], [acrylonitrile] and [MnSO₄] concentrations

[2-Amino-4-(methylthio)-butanoic acid] = 10.0 × 10⁻³ mol dm⁻³,
 [HClO₄] = 5.00 × 10⁻³ mol dm⁻³,
 Temperature = 308 K,
 [QNFC] = 1.0 × 10⁻³ mol dm⁻³,
 Solvent = 50-50 (% v/v) AcOH-H₂O,
 Diazophen] = 15.0 × 10⁻³ mol dm⁻³,

10 ⁴ [NaClO ₄] (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)	10 ⁴ [Acrylonitrile] (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)	10 ⁴ [MnSO ₄] (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)
0.00	5.75	0.00	5.75	0.00	5.75
0.50	5.52	0.50	5.68	0.50	5.84
0.75	5.36	0.75	5.66	0.75	5.92
1.00	4.82	1.00	5.70	1.00	5.98

3.7. Rate dependence on different catalysts

The reactions were carried out in the presence of different complexing agents like 4,5-diazophenanthrene, oxalic acid and 2,2'-bipyridyl under identical experimental conditions employed in the 4,5-diazophenanthrene catalyzed reaction and the reactivities were compared in Table 7. The order of catalytic efficiency is 2,2'-bipyridyl < oxalic acid < 4,5-diazophenanthrene. More pronounced activity is observed with 4,5-diazophenanthrene as a catalyst. This may probably due to the formation of more reactive electrophile in between oxidant and 4,5-diazophenanthrene and the corresponding transition state is well established.

Table 7. Rate constant for the oxidation of 2-amino-4-(methylthio)butanoic acid by QNFC in the presence of various complexing agents

[2-Amino-4-(methylthio)-butanoic acid] = 10.0 × 10⁻³ mol dm⁻³,
 [QNFC] = 1.0 × 10⁻³ mol dm⁻³,
 [HClO₄] = 5.0 × 10⁻³ mol dm⁻³,
 Solvent = 50-50 (% v/v) AcOH-H₂O, Temperature = 308 K,

Catalyst	10 ³ [catalyst] (mol dm ⁻³)	10 ⁴ k _{obs} (s ⁻¹)
4,5-Diazophenanthrene	15.0	5.75
Oxalic acid	15.0	4.91
2,2'-Bipyridyl	15.0	3.96

3.8. Rate dependence on different oxidants

The reactions were carried out in the presence of different oxidizing agents *viz.*, BIFC, QNFC, PFC and NDC and keeping all other reactant concentrations constant, the measured rate constant values were given in Table 8. The observed results show that both BIFC and QNFC show higher oxidizing efficiency.

Table 8. Rate constants for the oxidation of 2-amino-4-(methylthio)butanoic acid with various chromium(VI) reagents

[2-Amino-4-(methylthio)-

butanoic acid] = $10.0 \times 10^{-3} \text{ mol dm}^{-3}$, [HClO₄] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$,

[4,5-Diazophen] = $15.0 \times 10^{-3} \text{ mol dm}^{-3}$, Solvent = 50-50(% v/v)AcOH-H₂O,

Temperature = 308 K,

Oxidant	10^3 [Oxidant] (mol dm ⁻³)	4,5-Diazophenanthrene catalyzed reaction
QNFC	1.00	5.75
BIFC	1.00	5.09
PFC	1.00	5.00
NDC	1.00	3.96

3.9. Effect of temperature

The reactions were carried out at four different temperatures *viz.*, 303, 308, 313 and 318 K and keeping all other reactant concentrations constant and the rate constants were calculated (Table 9). The thermodynamic parameters were calculated from the Eyring's plot of $\ln k_{\text{obs}}/T$ versus $1/T$ (Fig.2) and are given in below. The oxidation reaction has been conducted at four different temperatures and the activation parameters were calculated. For 4,5-diazophenanthrene catalyzed reaction $\Delta H^\ddagger = 26.27 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -210.39 \text{ J K}^{-1} \text{ mol}^{-1}$.

Table 9. Effect of temperature on reaction rates

[2-Amino-4-(methylthio)-

butanoic acid] = $10.0 \times 10^{-3} \text{ mol dm}^{-3}$,

[HClO₄] = $1.50 \times 10^{-3} \text{ mol dm}^{-3}$,

[4,5-Diazophen] = $15.0 \times 10^{-3} \text{ mol dm}^{-3}$,

Solvent = 50-50(% v/v)AcOH-H₂O,

Temperature = 308 K,

Temperature (K)	$10^4 k_{\text{obs}}$ (s ⁻¹)
303	2.65
308	5.75
313	7.38
318	9.40

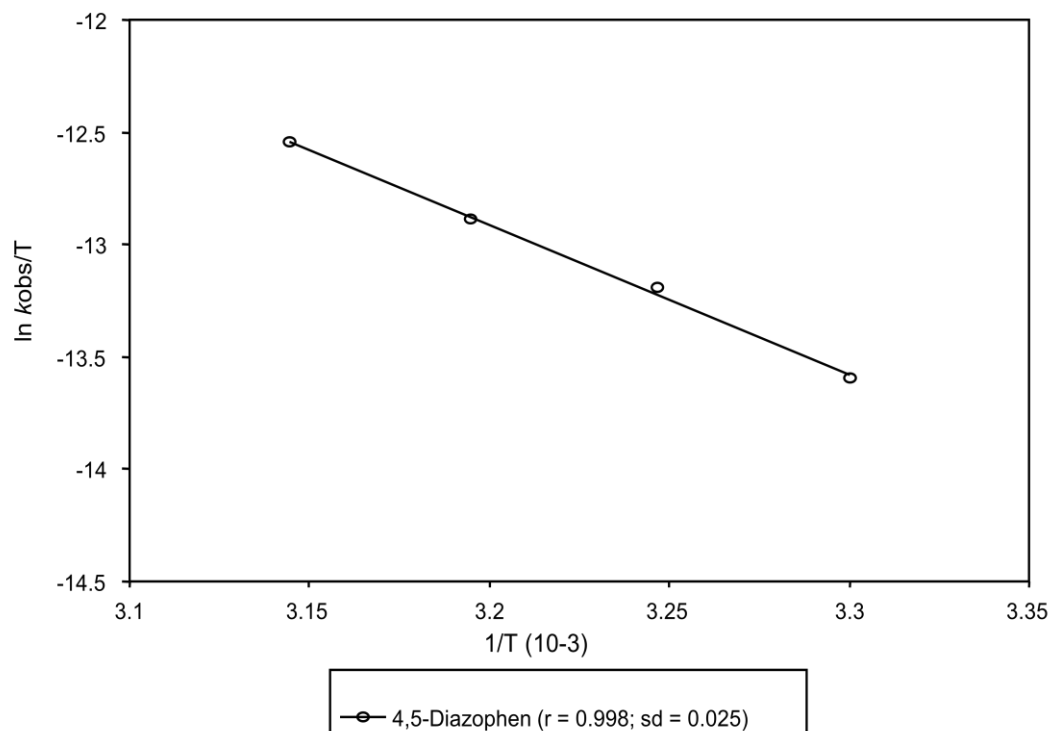
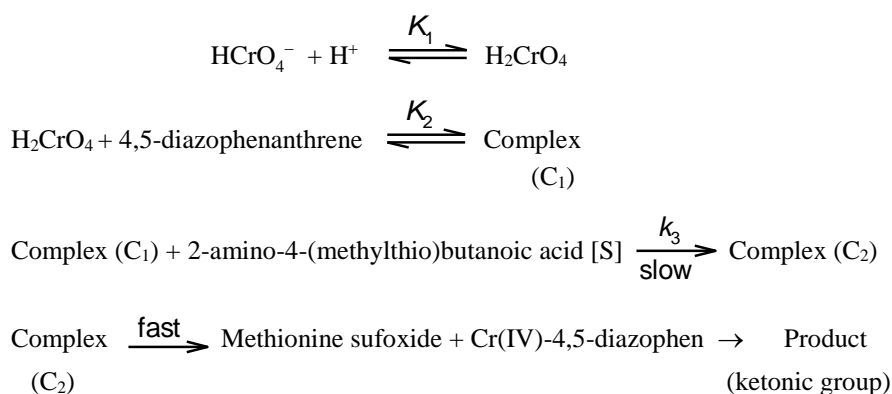


Fig. 2. Plot of $\ln k_{\text{obs}}/T$ versus $1/T$

3.10. Mechanism and rate law:

4,5-Diazophenanthrene catalyzed oxidation of 2-amino-4-(methylthio)-butanoic acid by QNFC:

From the observed kinetic results the following mechanism has been proposed. The effective oxidizing species HCrO_4^- protonates to give H_2CrO_4 in the equilibrium step. Further H_2CrO_4 react with 4,5-diazophenanthrene to given complex (C_1), then this C_1 reacts with substrate molecule to yield a complex (C_2). The complex C_2 dissociate to yield the product in the slow and rate-determining step.



The proposed mechanism has been characterized with the following rate law

Rate law =

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{K_1 K_2 k_3 [2\text{-amino-4-(methylthio)butanoic acid}][4,5\text{-diazophen}][\text{Cr(VI)}][\text{H}^+]}{\{1 + K_1[\text{H}^+]\}}$$

APPLICATION

Oxidation reaction has been a subject of major importance to many chemists and elucidation of the mechanism is undoubtedly one of the most fascinating problems in the mind of chemists.

CONCLUSION

The reaction is carried out in aqueous acetic acid medium at 308 K and the following results were obtained. Unit order dependence with respect to [QNFC] [2-amino-4-(methylthio)butanoic acid] [4,5-Diazophen] and the fractional order [H⁺] has been observed. Increase in the percentage of acetic acid increases the rate of the reaction. Added acrylonitrile has no effect on the reaction rate, ruling out the possibility of free radical pathway mechanism. The oxidation reaction has been conducted at four different temperatures and the activation parameters were calculated. For 4,5-diazophenanthrene catalyzed reaction $\Delta H^\ddagger = 26.27 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -210.39 \text{ J K}^{-1} \text{ mol}^{-1}$. The reaction is characterized by low enthalpy of activation and negative entropy of activation.

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