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Comparison of Kinetics and Mechanism for oxidation of 2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one by Mn(IV) and Mn(VII) Ion

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Abstract- *Kinetics of oxidation of 2, 6 Diphenyl-Piperidine-4-one and 3-Methyl 2, 6 Diphenyl-Piperidine-4-one by Mn (IV) and Mn (VII) in acidic medium exposes that reactions are of first order reaction. In this work it was noticed that rate of reaction and acid concentration are directly proportional to each other. The presence of 3-methyl substituent decreases the rate of oxidation with Mn (IV) and Mn (VII). The results are rational by a mechanism involving intermediate products. On the basis of result is clear that the rate of oxidation is higher by Mn(IV) than Mn(VII) in case of 2, 6 Diphenyl-Piperidine-4-one than 3-Methyl 2, 6 Diphenyl-Piperidine-4-one.*

Keywords- *Acidic medium, Kinetics, Oxidation, 2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one, Mn (IV), Mn (VII)*

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I. Introduction

Most of the information related to the reaction mechanism comes from chemical kinetics[1]. Kinetic study of redox reactions in aqueous organic solvents and the succeeding correlation of the reaction rates with different solvent parameters give important information concerning the mechanism of such reactions[2]. Kinetic studies on the oxidation of acids[3], cyclohexnol, allylalcohol, dimethyl sulpoxide and substituted aniline by N-chloro-3-methyl-2, 6- diphenylpiperidine-4-one have been reported[4]. The kinetics of oxidation of diphenylmethane by permanganate was given by[5] and they decided that more than one manganese ions are involved in the oxidation. Manganese (III) has been generally used for the oxidation of a many compounds together with carboxylic acids hydrocarbons, and hydroxyl compounds[6]. The transition and inner-transition metals of d and f orbital show different oxidation states and form metal complexes[7, 8]. Due to the presence of vacant d-orbital, these transition metal forms large number of coordination compound with ligands according to their electronic configuration[9]. Manganese dioxide (tetravalent) is known as an oxidizing agent[10]. The mechanism and kinetics for the oxidation of cyclohexanone by Mn (VII) and Mn (III) has been explained by J.S Littler[11-13]. In this report, comparison for mechanism in acidic medium for the oxidation of 2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one by Mn (IV) and Mn (VII) has been represented.

II. Material and Method

2,6-Diphenyl-Piperidine-4-one and 3-Methyl 2,6-Diphenyl-Piperidine-4-one, both were prepared in distilled water according to[14]. $KMnO_4$, H_2SO_4 and Na_2SO_4 were used without further purification. All other chemicals like acids and solvents used in this research work were of analytical grade. For the preparation of 0.05 M solution of Mn(IV) and Mn(VII)[15] approximately 7.8 g of potassium permanganate was mixed in 9.0 Molar H_2SO_4 with energetic stirring by a magnetic stirrer for a period of 7-8 hours. The solution was left for 10-12 hours and made up to 1 litre with 9 M H_2SO_4. Titrimetrically method was used to determine manganese (IV) solution[16] with the help of Ferric sulphate solution. For the determination of end point Ferrion indicator was used.

Stoichiomety determination: It was determined by calculating the concentration of Mn(IV) and Mn(VII) in samples by titration. The concentration of Mn(IV) and Mn(VII) was calculated after different time intervals to get the stoichiometry as a function of time. Before running samples into the stoichiometric, the initial concentration of Mn(IV) and Mn(VII) was always determined. Table no1shows the stoichiometry ratio for oxidant and substrate was noticed approx 2:1 for Mn(IV) and it was found to be 4:1 for Mn(VII).

Temperature 35^0C, I = 1.8M,
Conc. of piperiodone = 6×10^{-5}M, $[H^+]$ = 0.5M
[Mn (IV)] = 6×10^{-4}M, [Mn (VII)] = 6×10^{-4}M

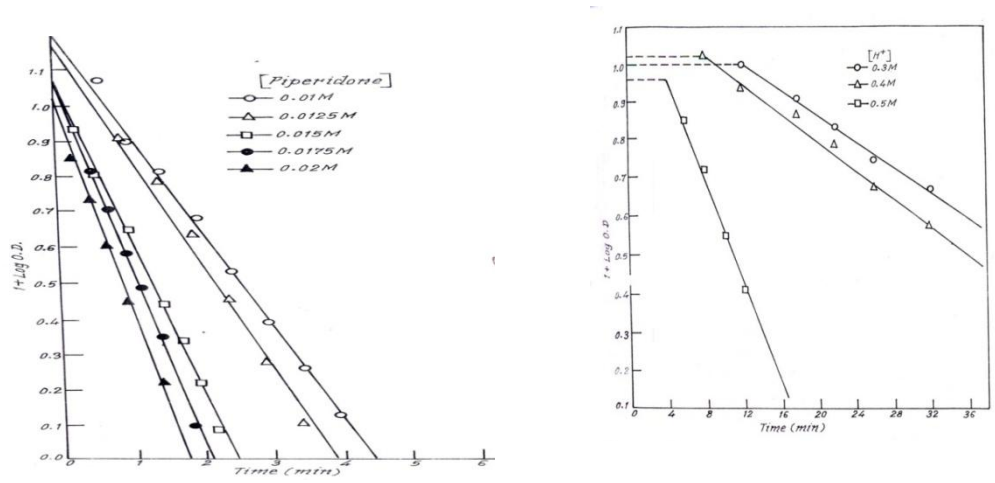
Table no 1

Time	$\frac{\Delta[\mathbf{Mn(IV)}]}{\Delta[\mathbf{Piperidine}]}$
5 hrs	0.952
20 hrs	1.258
25 hrs	2.069
Time	$\frac{\Delta[\mathbf{Mn(VII)}]}{\Delta[\mathbf{Piperidine}]}$
18hrs 30 min	3.67
48 hrs	4.40

Oxidation product and Kinetic Measurement: Mn(IV) solution was mixed with acidic solution of piperidone and Na_2CO_3 solution mixed drop by drop into this solution for neutralization. After cooling it alcohol was mixed and precipitates separated out with the help of ether. Similar process was repeated for Mn(VII). After analysis it was found that oxidation product was an acid. Kinetic Measurements for both were carried out spectrophotometrically at different range as 525 nm, 420nm and 380nm by using an S.P 700/500 spectrophotometer[17]. It was noticed that the rate of disappearance of both Mn(IV) and Mn(VII) was found to be first order in the presence of excess (30 times) of piperidone. Different Concentration of piperidine from 0.01 M - 0.02M was used, and the measurements were carried out at three different acidic ranges between 0.3M and 0.5M, at constant ionic strength 1.8 M after the addition of Na_2SO_4 solution.

III. Result and Discussion

Kinetics and mechanism of oxidation of 2,6-diphenyl piperidine-4-one and 3- methyl 2,6-diphenyl pipridine- 4-one by Mn(IV) in acidic medium have been examined. The graph of 1+ log O.D v/s time is linear for both metallic ions (fig.1 a and b).



(a) (b)

Fig.1a & b: Plots of 1+ Log O.D. against time for 2, 6-diphenyl piperidine-4-one oxidation by Mn (IV) and Mn(VII) at 55℃,
I = 1.8M, $[H^+]$ = 0.5M

The value of K_0 at various acidities is collected in Table no 2(a and b). In both the cases it was noticed that the reaction is formed to be first order with respect to oxidant. The first order nature with respect to oxidant is established from the reliability in the rate constant at different initial concentration of oxidant.

Table no 2a

Value of rate constants $k_o \times 10^4$ sec $^{-1}$ for the oxidation of 2, 6-diphenyl piperidine-4-one at I= 1.8 M and [Mn(IV)] = [Mn(VII)] = 6×10^{-4} M

Temp.° C	**[piperidone] $\times 10^2$ M**	**$[H_2SO_4]$ M for Mn(IV)**			**$[H_2SO_4]$ M for Mn(VII)**		
		0.3	**0.4**	**0.5**	**0.3**	**0.4**	**0.5**
35	1.00	-	14.17	18.21	3.95	7.05	10.11
	1.25	-	16.57	24.52	5.13	6.02	13.30
	1.50	16.47	18.97	30.40	6.30	9.00	16.50
	1.75	17.63	21.37	34.24	4.47	10.00	19.65
	2.00	18.81	28.30	38.19	8.65	11.94	23.00

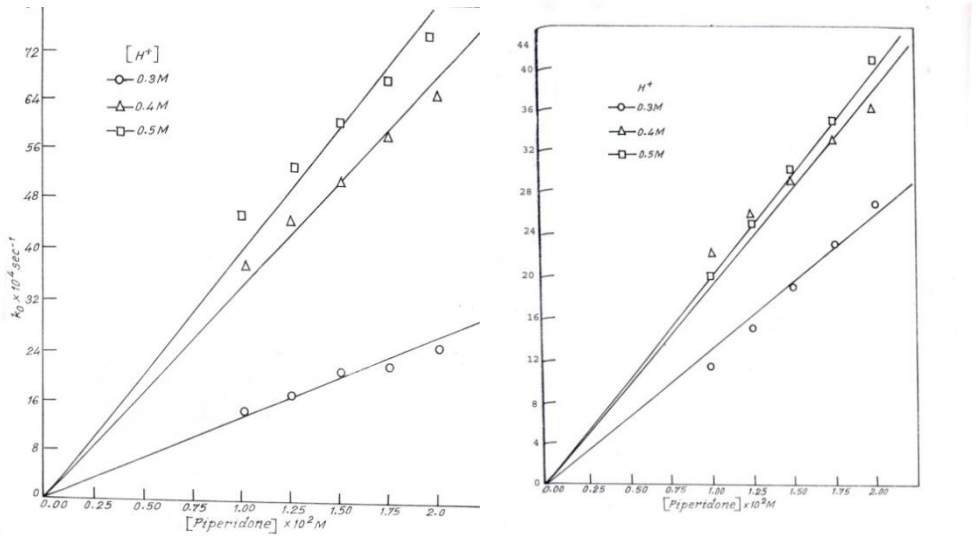
45	1.00	14.58	39.11	48.31	7.62	8.74	27.93
	1.25	17.08	45.45	54.80	10.50	12.32	33.05
	1.50	19.54	51.77	61.29	13.36	15.91	38.17
	1.75	22.01	58.07	67.79	16.23	19.50	43.30
	2.00	24.49	64.39	74.29	19.10	23.09	48.41
55	1.00	73.72	80.97	108.49	25.25	35.00	53.40
	1.25	81.63	90.79	126.14	32.78	38.43	66.11
	1.50	89.50	100.49	143.77	40.03	41.87	78.82
	1.75	97.49	110.39	161.38	47.30	45.30	91.53
	2.00	105.29	120.21	178.90	54.54	-	104.23

Table no 2b

Value of rate constants $k_o \times 10^4$ sec $^{-1}$ for the oxidation of 3-methyl-2, 6-diphenyl piperidine-4-one at I= 1.8 M and [Mn(IV)] = Mn(VII) = 6×10^{-4} M

Temp.° C	[piperidone] $\times 10^2$ M	$[H_2SO_4]$ M for Mn(IV)			$[H_2SO_4]$ M for Mn(VII)		
		0.3	0.4	0.5	0.3	0.4	0.5
35	1.00	12.85	11.81	14.40	3.32	7.09	8.07
	1.25	15.09	14.99	19.20	4.56	7.82	14.40
	1.50	17.31	18.20	23.93	5.81	8.56	20.74
	1.75	19.49	21.35	28.70	7.05	9.30	27.08
	2.00	21.72	24.55	33.57	8.30	10.02	33.41
45	1.00	26.37	28.80	37.85	11.33	22.97	20.31
	1.25	32.89	40.94	43.34	15.28	26.23	25.50
	1.50	39.41	48.83	53.07	19.23	29.50	30.68
	1.75	45.95	54.31	65.23	23.18	32.76	35.86
	2.00	52.45	59.81	77.37	27.12	36.02	41.04
55	1.00	52.59	71.15	68.61	35.37	31.38	44.94
	1.25	64.98	85.54	86.35	38.30	37.75	59.05
	1.50	77.34	100.00	104.12	41.21	44.11	73.16
	1.75	89.74	114.21	121.83	44.13	50.48	87.27
	2.00	102.12	128.67	139.57	47.05	56.85	101.38

Effect of changing concentration of piperidones: The piperidone concentration was changed from 0.01 -0.02 M, keeping the concentration of Mn(IV) and Mn(VII) constant. Study of rate constant indicates that the K_0 values increased noticeable with increasing concentration of piperidones. Table no 2a and 2b show values of K_0 at various acidities are composed for both Mn(IV) and Mn(VII). The graph of K_0 against concentration of piperidone at constant acidity and ionic strength were found to be linear (fig. 2a, 2b), hence the reaction is Ist order in piperidone.



(a) (b)

Fig.2 a &b: Plots of K_{obs} against [3-methyl- 2, 6 diphenyl piperidine-4-one] M at 45˚C with Mn(IV) and Mn(VII) respectively

Table no 3a and 3b show bimolecular rate constants K_2 have been considered from the slops of these straight lines at I = 1.8M.

Table no 3a

Bimolecular rate constants $K_0 \times 10^2 L\ M^{-1}\ sec^{-1}$ for the oxidation of 2,6-diphenyl piperidine-4-one

Temp.° C	$[H_2SO_4]$ M for Mn(IV)			$[H_2SO_4]$ M for Mn(VII)		
	0.3	**0.4**	**0.5**	**0.3**	**0.4**	**0.5**
25	2.30	3.05	3.35	2.6	3.60	3.70
35	8.85	12.76	19.01	2.94	4.98	20.72
45	21.90	26.05	48.53	11.67	13.04	25.00
55	49.55	57.54	70.99	15.79	25.47	56.43

Table no 3b

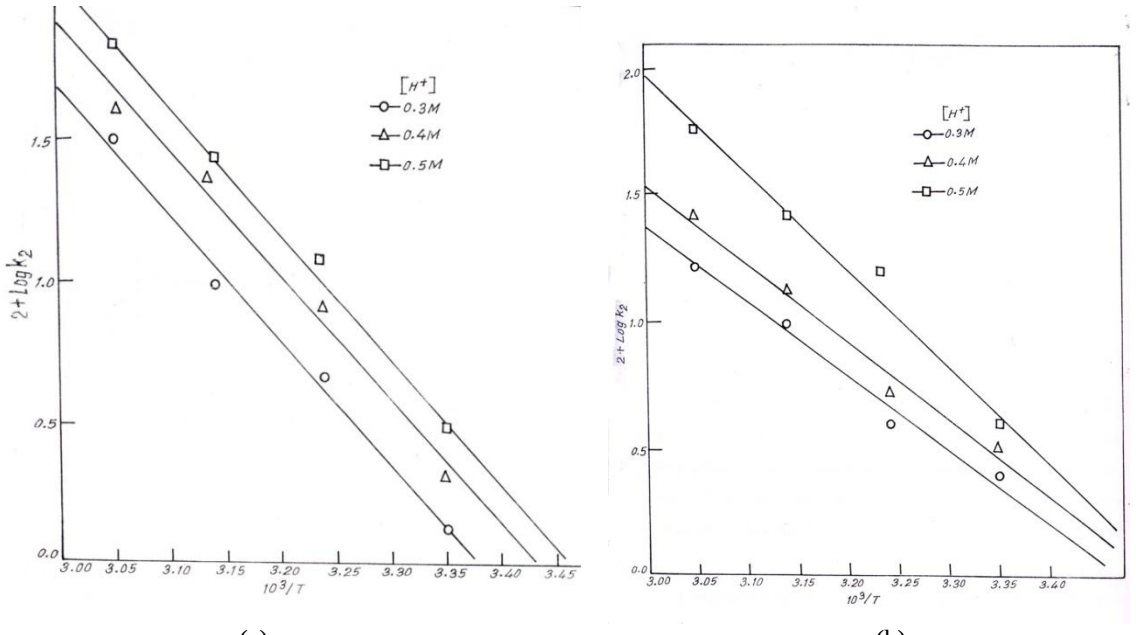
Bimolecular rate constants $K_0 \times 10^2 L\ M^{-1}\ sec^{-1}$ for the oxidation of 3-methyl- 2,6-diphenyl piperidine-4-one

Temp.° C	$[H_2SO_4]$ M for Mn(IV)			$[H_2SO_4]$ M for Mn(VII)		
	0.3	**0.4**	**0.5**	**0.3**	**0.4**	**0.5**
25	1.37	2.78	3.09	-	-	-
35	4.63	9.53	10.32	4.69	3.89	12.78
45	9.93	25.24	25.97	11.48	14.35	20.47
55	31.64	39.25	60.47	13.74	29.02	50.83

There is no spectroscopic confirmation for the formation of Mn(VII) piperidones complexes as no changes in the absorption spectrum of Mn(VII) on the addition of piperidones while slow changes of absorption take place due to oxidation.

Effect of concentration of acid on reaction rate: Table no 3a and 3b shows kinetics of oxidation of the substituted piperidones has been studied in different acidity ranges 0.3- 0.5 M. It was noticed that the rate of reaction increases with increasing acid concentration.

Effect of temperature on reaction rate: The oxidation rate of 2,6-diphenyl piperedine-4-one and 3 methyl 2,6-diphenyl piperedine-4-one with Mn(IV) and Mn(VII) have been calculated at different temperatures in the range 25- 55℃. It was noticed that the rate of reaction increases with increasing temperature. The activation parameters have been calculated from the linear Arrhenius plot (fig. 3a, 3b) of log K_2 vs T^{-1}.



(a) (b)

Fig.3a and b: Arrhenius plots for 2,6-diphenyl piperidine-4-one oxidation with Mn(IV) and Mn(VII) respectively

Activation parameters: Table no 4a and 4b show linear plot obtained for log K_2 against 1/T. The values of ΔE_a, ΔH^*, ΔS^* and ΔG^* were calculated.

Table no 4a

Values of activation parameters for the oxidation of 2,6-diphenyl piperidine-4-one

$[H_2SO_4]$ M	ΔE_a kJ mole^{-1}	ΔH^* kJ mole^{-1}	ΔS^* JK^{-1} mole^{-1}	ΔG^* kJ mole^{-1}
Mn(IV)				
0.3	67.55 ± 0.72	67.39 ± 0.72	−14.24 ± 3.73	81.59 ± 1.36
0.4	78.92 ± 1.13	81.41 ± 1.13	−0.83 ± 2.25	81.65 ± 2.35
0.5	89.90 ± 2.45	81.41 ± 2.45	6.63 ± 7.82	82.06 ± 4.89
Mn(VII)				
0.3	46.65±2.17	44.05±2.17	−95.76±7.26	83.22±4.33
0.4	74.57±1.58	72.00±1.55	−97.40±4.29	83.80±3.14
0.5	91.54±1.58	88.95±1.57	−34.40±5.47	80.80±3.14

Table no 4b

Values of activation parameters for the oxidation of 3-methyl-2,6-diphenyl piperidine-4-one

$[H_2SO_4]$ M	ΔE_a kJ mole^{-1}	ΔH^* kJ mole^{-1}	ΔS^* JK^{-1} mole^{-1}	ΔG^* kJ mole^{-1}
Mn(IV)				
0.3	85.64 ± 0.95	79.51 ± 0.95	−10.15 ± 6.25	83.25 ± 1.86
0.4	82.10 ± 1.89	83.11 ± 1.89	−1.74 ± 3.03	81.59 ± 3.64
0.5	85.52 ± 2.23	82.97 ± 0.95	4.75 ± 8.15	81.41 ± 1.81
Mn(VII)				
0.3	56.34±2.32	53.75±2.22	−131.08±7.03	84.44±4.44
0.4	56.38±1.32	53.84±1.32	−36.40±5.10	81.18±2.64
0.5	70.22±2.33	67.60±2.33	30.47±4.05	81.10±4.66

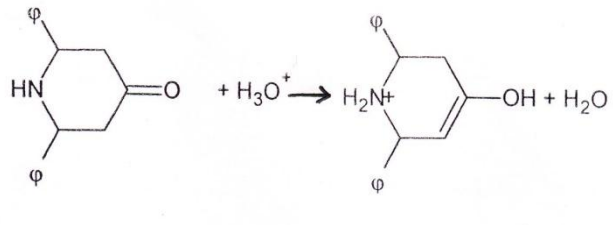
Rate law: On the basis of experimental data given above in tables the rate expression for Mn(IV) can be given as:

$$[Mn(OH)_3]^+ \rightarrow MnO_2 + H_2O + H^+$$

$$-\frac{d[Mn(IV)]}{dt} = k\,[\text{piperidone}]\,[Mn^{+4}]\,[H^+]$$

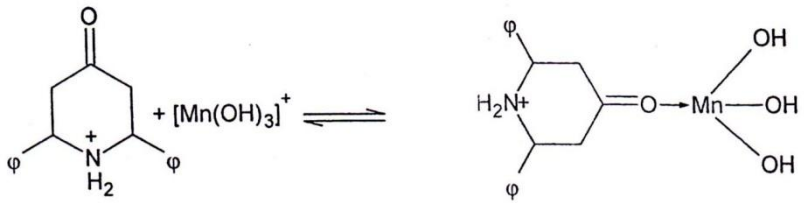
For Mn(VII) :

$$MnO_4^- + H_3O^+ \rightleftharpoons HMnO_4 + H_2O$$

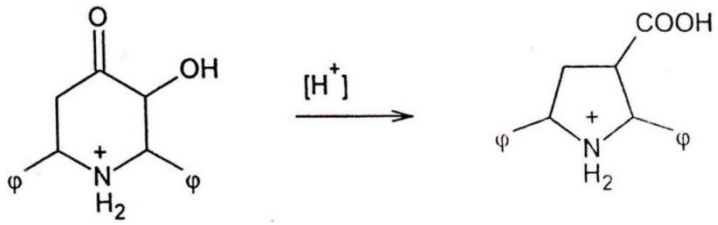


$$\frac{d[Mn(VII)]}{dt} = k\,[\text{piperidone}]\,[HMnO_4]\,[H^+]$$

Mechanism of oxidation: It is difficult to dissolve MNO_2 (Mn in oxidation state IV) in acids, the best method suggested for prepration of Mn(IV) solution is by reduction of $KMnO_4$ in acid medium. Further an aged solution of Mn(IV) in sulphuric acid prepared by above method gives a precipitate of MnO_2. This means in a freshly reduced solution of KMnO4, Mn(IV) as $Mn(OH)_3^+$ are the dominant species. Hence we have assumed that $Mn(OH)_3^+$ as the attacking species. So the following mechanism could be proposed for Mn(IV) oxidation.



All the above facts shows that the oxidation proceeds through the formation of cations and the mechanism of piperidone with Mn(VII) can be given as-



Oxidation rate of 2, 6- diphenyl piperidine-4-one and 3-methyl-2, 6- diphenyl piperidine-4-one: An evaluation of the oxidation state of 2, 6- diphenyl piperidine with or without 3-alkyl substituent during the basis of oxidation with Mn(IV) and Mn(VII) expose that the rate of oxidation of the former is higher than that of the 3-alkyl substituent, table no 5.

Table no 5

Rate constants for the oxidation of 2, 6- diphenyl piperidine-4-one and 3-methyl-2, 6- diphenyl piperidine-4-one by Mn(IV) and Mn(VII)

piperidone	H_2SO_4	Oxidant	
		Mn(IV)	Mn(VII)
2,6- diphenyl piperidine-4-one	0.3	49.5	16.0
	0.4	57.5	25.5
	0.5	71.0	56.5
3-methyl-2,6-diphenyl piperidine-4-one	0.3	32.0	14.0
	0.4	39.0	29.0
	0.5	60.0	51.0

In the present study the rate constant value is decreased by the introduction of methyl group at 3 positions in the piperidine ring system.

IV. Conclusion

The present investigation have been successful in the determining the mechanism of oxidation of substituted piperidones by Mn(IV) and Mn(VII) in acidic medium. The acid permanganate seems to be the active species in case of Mn(VII) and Mn(IV) as $Mn(OH)_3^+$. The rate of oxidation for the substituted piperidone is more in case of 2, 6-di phenylpiperidine-4-one than 3 methyl 2, 6 di-phenyl piperidine - 4-one. On the basis of result is clear that the rate of oxidation is higher by Mn(IV) than Mn(VII).

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