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Oxidation of Benzyl Alcohol by Quinolinium Bromochromate

Seplapatty Kalimuthu Periyasamy

Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli, Tamilnadu, India.

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ABSTRACT

Quinolinium bromochromate (QBC) oxidizes benzyl alcohol and in the presence of acid to give aldehyde. The reaction is showing first order dependence on [oxidant] and [H^+] ion and fractional order dependence with respect to [substrate].The rate increases with decrease in the dielectric constant of the medium and increase in ionic strength has negligible effect on the rate. The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway. The added Mn^{2+} increases with decrease the reaction rate to involve the two electron transfer process involved in the reaction. A suitable mechanism is proposed.

Keywords: Quinolinium bromochromate, Benzyl alcohol Oxidation, Kinetics and Mechanism.

1. INTRODUCTION

Quinolinium bromochromate (QBC) has been used as a mild and selective oxidizing reagent in synthetic organic chemistry.[1] There seems to be no reports on the kinetic and mechanistic aspects of oxidation reactions by QBC. The kinetics of oxidation of alcohols by QBC has also not been reported. We have been interested in the kinetics of reactions of complexed Cr(VI) species and have already reported such studies of the oxidation of primary aliphatic alcohols by other pyridinium and quinolinium halochromates.[2–4] We have been interested in the synthesis and kinetics of reactions of complexed Cr(VI) species[5] and have reported the kinetics and mechanism of oxidation of benzyl alcohol by potassium chlorochromate[6] and quinolinium chlorochromate[7]. Recently we prepared quinolinium bromochromate (QBC)[8], which in readily oxidizes aliphatic primary alcohols to the corresponding carbonyl compounds. Here, we examine the kinetics and mechanism of this oxidation of benzyl alcohol with QBC in aqueous acetic acid medium.

2. EXPERIMENTAL

2.1 Materials

QBC was prepared by the reported method[1] and its purity was checked by iodometry.

Procedures used for the purification of the alcohols have been described earlier.[9]

Acetic acid

The procedure followed for the purification of acetic acid was essentially similar to that of Weissberger[10]. Glacial acetic acid (AR) 2 litre was partially frozen and about one litre of the liquid was removed. The residue was melted and refluxed with chromium trioxide (30 g) for 4 h and fractionally distilled. The portion distilling between 116-118 °C was collected, partially frozen and about half of the acid was discarded as liquid. The remaining residue was melted and fractionated again after treating with chromium trioxide (30 g). The fraction boiling at 116-118 °C was collected and kept in brown bottles.

Water

Deionised water was distilled twice in ‘corning’ glass vessels, the second distillation being from alkaline potassium permanganate and was used throughout the kinetic measurements.

Other reagents

Sodium perchlorate, perchloric acid, sodium thiosulphate, manganous sulphate, acrylonitrile, potassium iodide and starch were all of AnalaR grade and were used as such.

Kinetic measurements

The reactions were performed in aqueous acetic acid medium under pseudo-first order conditions by maintaining a large excess of substrate over quinolinium bromochromate. The kinetic measurements were carried out spectrophotometrically in a thermostated cell compartment of a spectrophotometer (Perkin Elmer-Lambda 35) at 470 nm. This wavelength of the maximum absorption due to quinolinium bromochromate has been observed and absorption due to other reaction species was negligible[11]. Oxidation reaction was studied only in the concentration range of quinolinium bromochromate where the Beer’s law is obeyed. The reactions were followed upto 70% completion. The rate constants were evaluated from the linear plot of log (absorbance) *versus* time by the least square method and were reproducible within 3%.

Stoichiometry and Product analysis

Reaction mixtures containing an excess of the oxidant over benzyl alcohol is kept at room temperature in presence of perchloric acid for two hours. Estimation of the unreacted oxidant proved that one mole of oxidant consumes one mole of substrate. The same experimental conditions were used for kinetic determinations; a solution of the reaction mixture was kept under nitrogen for 24 h. The solution was extracted with ether, the organic layer washed with water was dried over anhydrous sodium sulphate and then concentrated. The product was benzaldehyde identified by spot tests, the product was confirmed by its 2:4 DNP derivative (80% yield) and silver mirror test. The products was further characterised by IR spectra and GC-MS. The following stoichiometric reaction obtained from experimental results are given below.

$$RCH_2OH + CrO_2BrO^-QH^+ \longrightarrow RCHO + (HO)_2CrBrO^-QH^+$$

3. RESULTS AND DISCUSSION

Kinetics and mechanism of oxidation of Benzyl alcohol by Quinolinium Bromochromate (QBC)

Effect of varying the [QBC]

The oxidation of benzyl alcohol by QBC was investigated at several initial concentrations of the oxidant [QBC]. (Table 1). At constant temperature and the [substrate] in excess, the plot of log absorbance *versus* time was linear indicating first order dependence of reaction on [QBC]. The values of the pseudo –first order rate constant (k_1) were evaluated from the plots, according to the first order equation by the method of least square, one representative graph has been given in (Fig 1).

Table-1

[Benzyl alcohol]=4.0×10^{-2} *moldm*$^{-3}$ AcOH-H_2O = 40:60(%) [H^+] =10.0×10^{-2}*moldm*$^{-3}$ Temperature=313K

[QBC]× 10^3 *mol dm*$^{-3}$	**$k_1\times10^4$ *s*$^{-1}$**
3.60	5.47
7.20	5.48
10.8	5.47
14.4	5.49
18.0	5.46

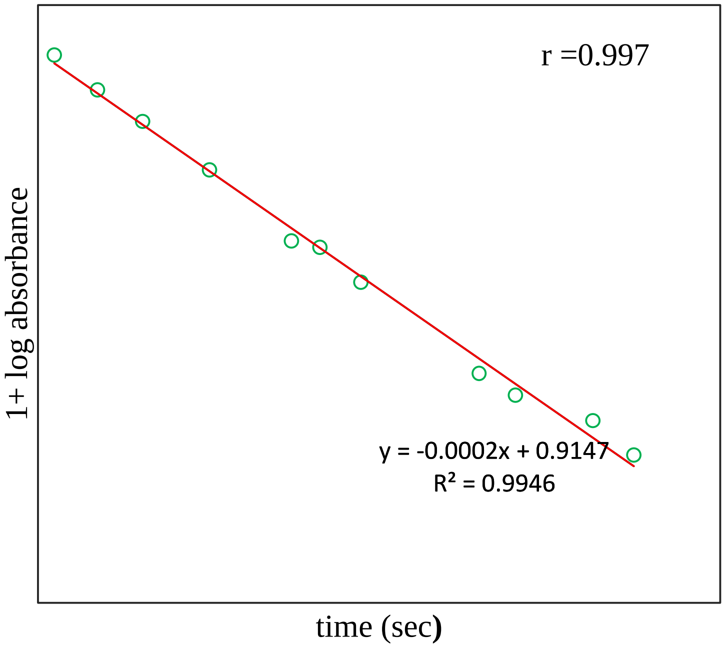


Fig.1. Plot of log absorbance versus time

Effect of varying the Substrate [Benzyl alcohol]

The concentration of benzyl alcohol is varied from 2.00 – 10.00×10^{-2} M at fixed concentration of the other reaction components. The rate of the reaction increases with increase in [substrate]. A plot of log k1 *versus* log [substrate] gives a straight line (Fig.2) with a fractional slope (b = 0.16), the correlation coefficient being 0.997.The rate of the oxidation is fractional order with respect to substrate. It was further well demonstrated by Michaelis-Menten's plot (Fig.3) which gives a definite intercept at the rate axis.

Table-2

[QBC]=7.20×10^{-3} *moldm*$^{-3}$ [H^+]=10.0×10^{-2} *moldm*$^{-3}$ AcOH-H_2O = 40:60(%) Temperature=313K

[Benzyl alcohol] ×10^2 *mol dm*$^{-3}$	**k_1×10^4** *s*$^{-1}$
2.00	4.87
4.00	5.47
6.00	5.88
8.00	6.08
10.00	6.25

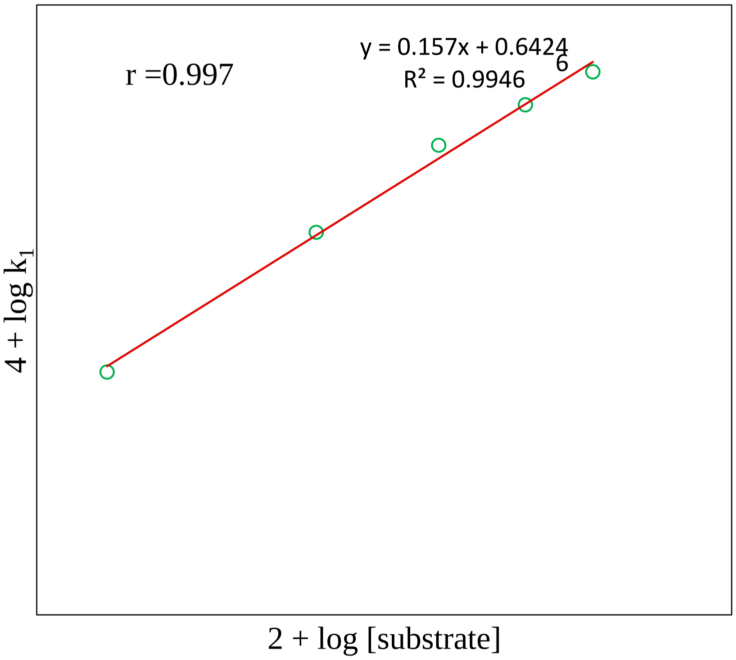


Fig.2. Plot of log k_1 *versus* log [substrate]

Effect of varying the ionic strength

The reaction was studied by varying the concentrations of sodium perchlorate and keeping the other variables constant. The results indicate that ionic strength has negligible effect on the reaction rate, which confirm the participation of an ion and neutral molecule in the rate determining step[12]

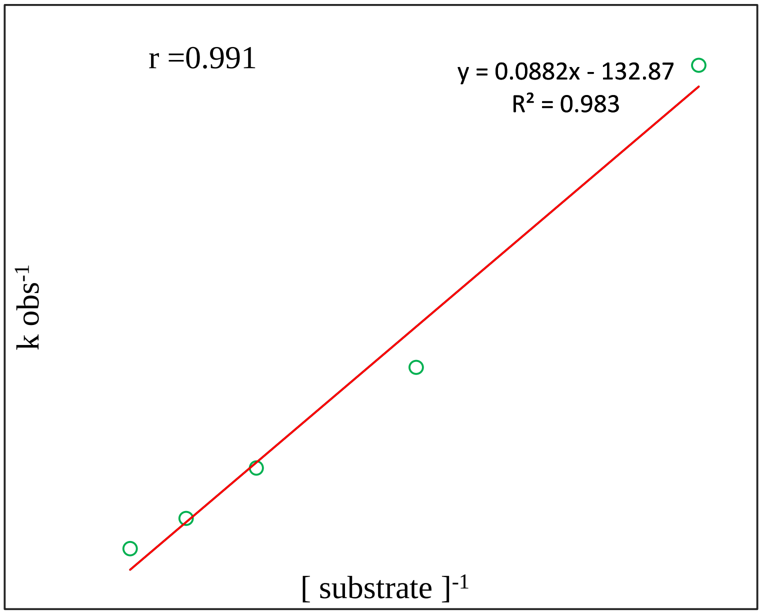


Fig.3. Michaelis-Menten's plot

Table-4

[QBC]=7.20×10^{-3} *moldm*$^{-3}$ [H^+] =10.00×10^{-2} *moldm*$^{-3}$ AcOH-H_2O = 40:60(%) [Benzyl alcohol]=4.00×10^{-2} *moldm*$^{-3}$ Temperature=313K

[$NaClO_4$] $\times10^4$ *mol dm*$^{-3}$	**$k_1\times10^4$ *s*$^{-1}$**
0.00	5.48
1.80	5.43
3.60	5.45
5.40	5.48
7.20	5.47

Effect of varying the hydrogen ion concentration

The reaction was carried out at different initial concentrations of perchloric acid while the other variables were kept constant. The rate constants were found to increase with increase in the concentration of perchloric acid. But, the plot of logk_1 versus log [H^+] was found to be linear. (Fig 5) with a slope of unity indicating first order dependence with respect to hydrogen ion concentration.

Table-5

[QBC]=7.20×10^{-3} *moldm*$^{-3}$ AcOH-H_2O = 40:60(%) [Benyl alcohol]=4.00×10^{-2} *moldm*$^{-3}$

Temperature=313K

[H^+] ×10^2 *mol dm*$^{-3}$	**k_1×10^4 *s*$^{-1}$**
5.00	3.39
10.00	5.48
15.00	7.73
20.00	10.59
25.00	12.88

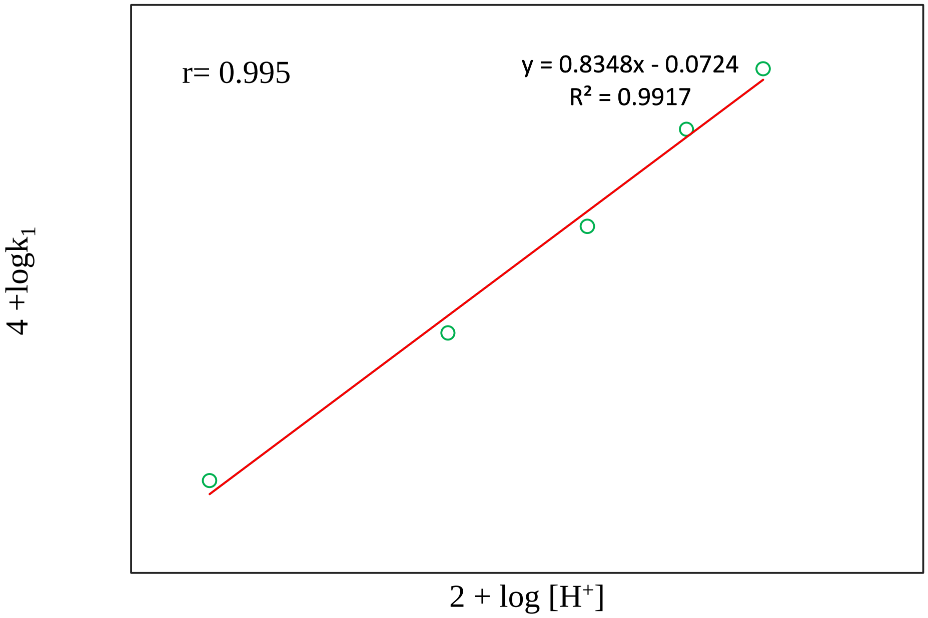


Fig.5. Plot of log k_1 *versus* log [H^+]

Effect of varying the solvent composition

The reaction rate was measured at different acetic acid -water mixtures. It was observed that an increase in the percentage of acetic acid considerably increased in the rate of the reaction. The plot of log k_1 *versus* D^{-1} gave a straight line with a positive slope[13] (Fig 6) suggests the involvement of an ion –dipole interaction in the rate determining step[14,15] .

Table -6

[QBC]=7.20×10^{-3} *moldm*$^{-3}$ [H^+] =10.00×10^{-2} *moldm*$^{-3}$ [Benzyl alcohol]=4.00×10^{-2} *moldm*$^{-3}$

AcOH-H_2O = 40:60(%) Temperature=313K

AcOH-H_2O %(v/v)	**D**	**k_1 10^4 s^{-1}**
30-70	57.85	5.01
40-60	50.46	5.47
50-50	43.08	6.17

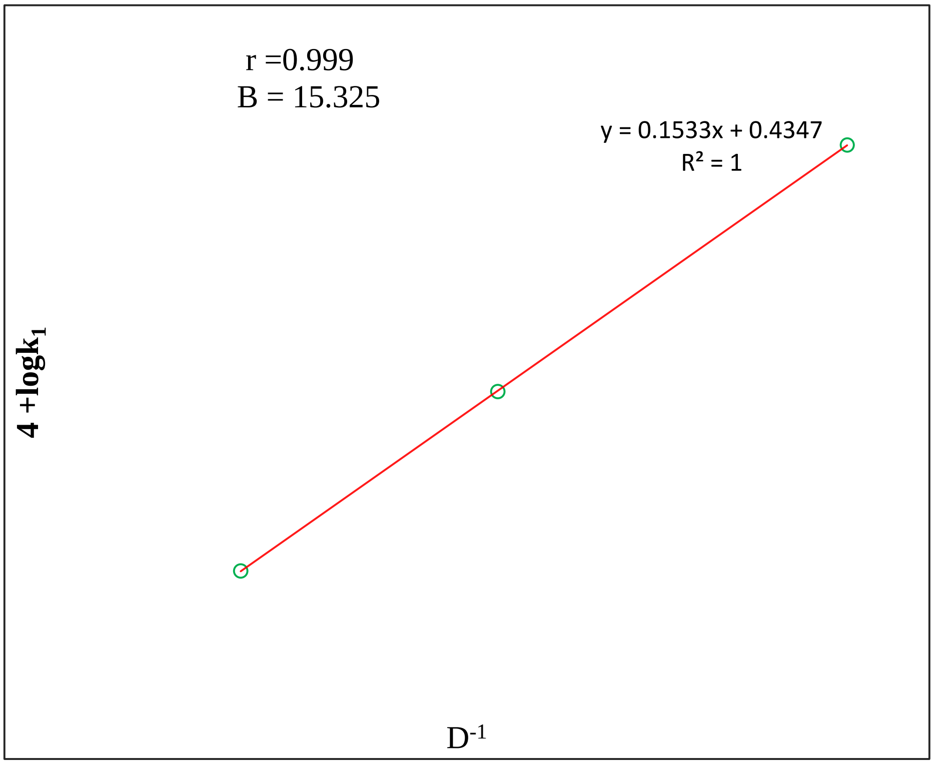


Fig.6. Plot of log k_1 *versus* D^{-1}

Effect of added acrylonitrile

The added acrylonitrile has no effect on the reaction mixture indicating the absence of free radical mechanism ,no turbidity was obtained.

Effect of varying the manganous sulphate

The reaction was carried out with the varying concentrations of Mn^{2+} ions keeping all the other factors constant The added Mn^{2+} ions has decreased the rate of the reaction[16-18]. It indicates that two electron process may be involved in the reaction (Table 7)

Table-7

[QBC]=7.20×10^{-3} *moldm*$^{-3}$ [H$^+$] =10.00×10^{-2} *moldm*$^{-3}$ [Benzyl alcohol]=4.00×10^{-2} *moldm*$^{-3}$

AcOH-H_2O = 40:60(%) Temperature=313K

[MnSO$_4$] ×10^4 *mol dm*$^{-3}$	**$k_1\times10^4$ *s*$^{-1}$**
0.00	5.48
1.80	5.00
3.60	4.96
5.40	4.55
7.20	4.00

Effect of varying the temperature

The reaction has been studied at four different temperatures keeping all other factors constant .The thermodynamic parameters have been computed[19, 20] from the linear plot of ln(k_2/T) *versus* 1/T using Eyring's equation (Fig.8)

$\Delta H^{\#}$ = 22.09 *kJmol*$^{-1}$

$\Delta S^{\#}$ = -210.29 *JK-1mol*$^{-1}$

$\Delta G^{\#}$ = 96.33 *kJmol*$^{-1}$

Ea = 24.69 *kJmol*$^{-1}$

Table-8

[QBC]=7.20×10^{-3} *moldm*$^{-3}$ [H$^+$] =10.00×10^{-2} *moldm*$^{-3}$ [Benzyl alcohol]=4.00×10^{-2} *moldm*$^{-3}$

AcOH-H_2O = 40:60(%)

Temperature K	**$k_1 10^4$ *s*$^{-1}$**
303	4.24
313	5.47
323	7.60
333	10.17

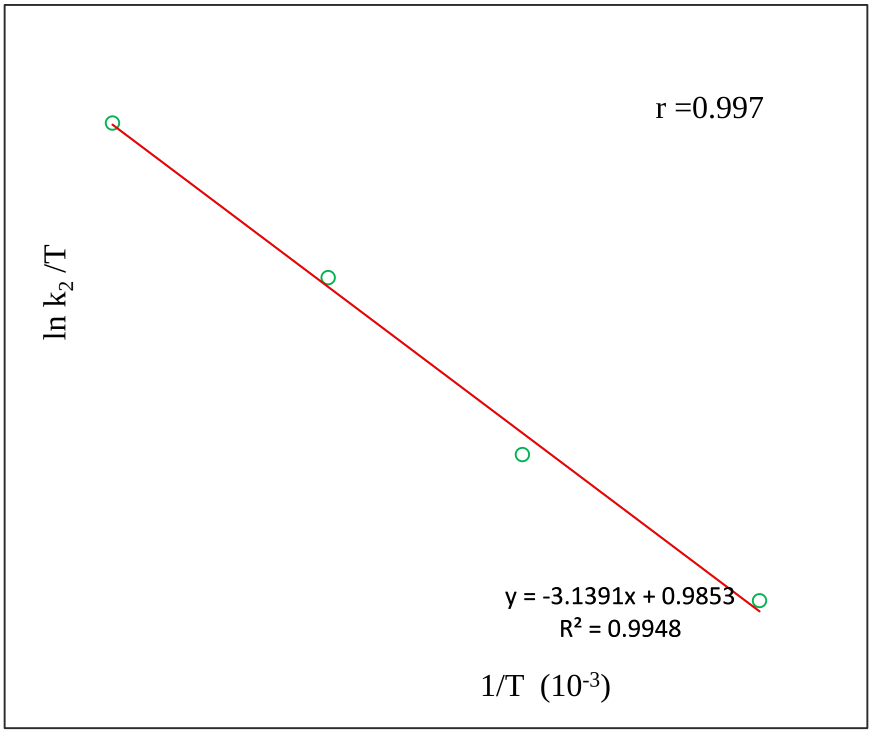


Fig.8. Plot of $\ln k_2/T$ *versus* 1/T

Mechanism

From the above observation it is clear that the reaction is showing first order dependence on [oxidant] and $[H^+]$ ion and fractional order dependence with respect to [substrate].

The rate increases with decrease in the dielectric constant of the medium and increase in ionic strength has negligible effect on the rate.

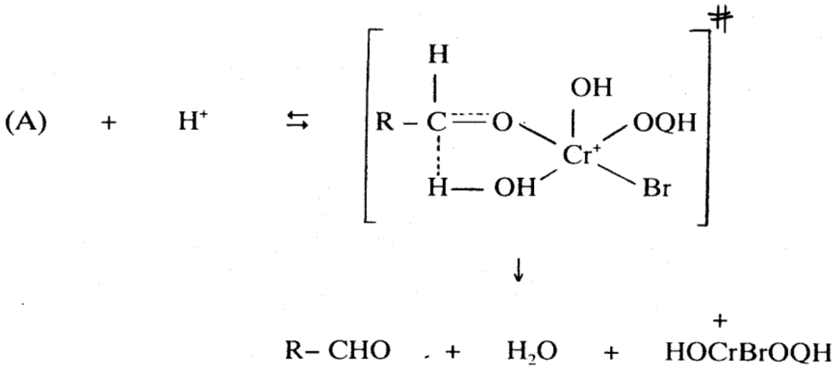
The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway. The added Mn^{2+} increases with decrease the reaction rate to involve the two electron transfer process involved in the reaction.

Based on the above fact the following mechanism is proposed for the oxidation of benzyl alcohol by quinolinium bromochromate (Scheme I)

Mechanism

$R - CH_2 - OH + CrBrOQHO_2 \rightleftharpoons \{R\text{-} CH_2 - O\text{-}CrBr\,O_2(QH)\text{-}(OH)\}$

$(R = C_6H_5)$



(Benzyl alcohol) (A)

(R = C6H5) (Benzaldehyde)

(Scheme I)

Rate law:

These above observations suggest that the rate law can be shown as

$$\text{Rate} = k_3 \text{ Complex}$$

$$= \frac{k_3 K_2 K_1 [O] [S] [H^+]}{1 + K_2 [S]}$$

4. CONCLUSION

The main product is found to be benzaldehyde. The reaction was first order each in [oxidant] and [H+] and fractional order dependence with respect to [substrate]. The stoichiometry was found to be one mole of benzyl alcohol consuming one mol of quinolinium bromochromate. The plots of log k, *versus* 1/D were found to be linear, with positive slopes. The negative values of S# provided support for the formation of a rigid activated complex. A mechanism in terms of active species of oxidant and catalyst is proposed and the rate law is derived and verified.

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