

Low-bromide containing MC catalyst for the autoxidation of *para*-xylene

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Abstract

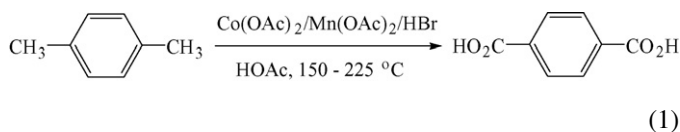
The autoxidation of *para*-xylene (pX) was carried out with the usual MC catalyst, $\text{Co}(\text{OAc})_2/\text{Mn}(\text{OAc})_2/\text{Br}^-$, in the presence of acid additives, but with significantly lower concentrations of bromide. However, the reaction came to a halt after only 15% of the theoretical uptake of oxygen had occurred, presumably due to the loss of inorganic bromide (Br^-) in the form of benzylic bromides. But, a tiny amount of $\text{Zn}(\text{OAc})_2$ restored the effectiveness of the catalyst, even with lower bromide, down to 0.28 mmol L^{-1} . Autoxidation of pX occurs by a chain mechanism that involves formation of the dibromide radical which abstracts a hydrogen atom from *para*-xylene to form the carbon-centered radical ArCH_2^\bullet . However, excess dibromide radicals are formed during fast chain reactions, which react with ArCH_2^\bullet to produce undesired benzylic bromides, in parallel with its involvement in the oxidation of substrates. It is believed that $\text{Zn}(\text{OAc})_2$ acts as a bromophilic agent and stores excess Br^- in the form of monobromozinc(II), and minimized the loss of Br^- .

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1. Introduction

The aerobic oxidation of *para*-xylene catalyzed by the MC catalyst is an important reaction for industrial scale production of terephthalic acid [1–4]. Terephthalic acid is used to manufacture poly(ethyleneterephthalate), a polymer commonly made into fibers, resins, films, etc. [5]. The MC catalyst is a combination of $\text{Co}(\text{OAc})_2$, a promoter (HBr) and a cocatalyst, $\text{Mn}(\text{OAc})_2$ [6–9].



Known for decades as being an effective promoter for the aerobic oxidation of hydrocarbons, bromide ion poses economic and environmental drawbacks [10]. Bromide ion corrodes expensive titanium-clad reactors and also forms methyl bromide, $\text{CH}_3\text{Br}(\text{g})$ [11], which must be sequestered because it can deplete the ozone layer [12,13]. But the catalyst becomes ineffective without use of the bromide promoter. Therefore,

a replacement of HBr promoter is highly desirable. Recently, *N*-hydroxyphthalimide (NHPI) and its ring-substituted derivatives have been reported to be highly efficient promoters for *para*-xylene oxidation [10,14], but they, too, are not without their problems. NHPI decomposes, particularly when the chain reaction is fast, and therefore, continuous addition of NHPI is recommended [14].

Our recent publication on this subject has demonstrated a significant improvement, in terms of rates and product yields, of the effectiveness of the MC catalyst in the presence of strong acid additives, such as trifluoroacetic acid, heptafluorobutyric acid and *p*-toluenesulfonic acid [15]. Only 5 wt% of acid additives accelerated the yield of terephthalic acid up to 15-fold. However, most reactions were carried out using 1:1 ratio of catalyst metals (15 mM) to bromide ions (15 mM). In this study, we describe the effectiveness of the MC catalyst using low concentration of bromide promoter in the presence of the strong acids, trifluoroacetic acid (TFA) and heptafluorobutyric acid (HFBA). Typical experiments have been carried out using 60 times lower bromide ion than previously reported. The ratio of total catalyst metals (20 mM) to bromide ion (0.28 mM) in our present study is 71:1. The effectiveness of the MC catalyst has also been studied in the presence of bromophilic agent, $\text{Zn}(\text{OAc})_2$. The conditions tested here are not, however, those used (nor presumably usable) in commercial practice.

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2. Experimental

2.1. Materials

The following reagents were used as obtained commercially without further purification: cobalt(II) acetate tetrahydrate, manganese(II) acetate, manganese(III) acetate, zinc(II) acetate, glacial acetic acid, trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA), sodium bromide, pX, *p*-tolualdehyde, *p*-toluic acid and terephthalaldehyde (TPA).

2.2. General oxidation procedures

The progress of the autoxidation reactions was monitored in HOAc by the oxygen uptake method using a manometric apparatus similar to the one described in the literature [1,14,16]. The heavy-walled glass reactor, which contains an impeller to maintain oxygen saturation of the solution, was thermostated at 70 °C by means of a circulating water bath. Oxygen consumption was measured by monitoring the decrease in volume, at constant 1 atm pressure of pure oxygen, in a burette connected to the reactor. The initial reaction rates were calculated from the slope of the linear plots of the volume of oxygen consumption against time.

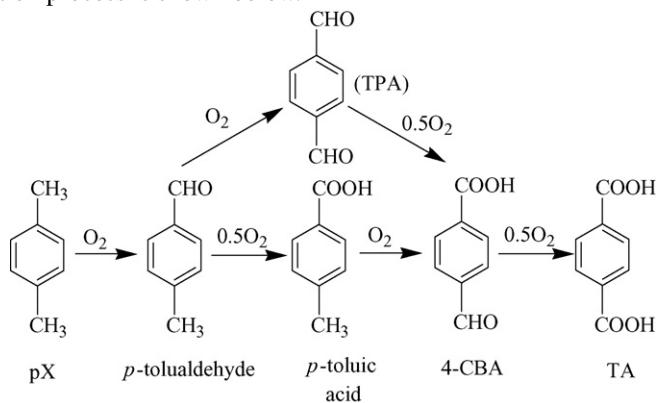
Even at 70 °C, these conditions lie in an explosive region. In addition to the sturdy reactor, the reactions were carried out inside a fume hood with a safety shield in front of the reactor. No explosions occurred during the course of this work.

3. Results

The oxidation of pX to terephthalic acid occurs through a multi-step process. The stoichiometric equation is given below [15].



Several partially oxidized forms of pX are produced as intermediates during the course of free radical chain reaction. These intermediates are *p*-tolualdehyde, *p*-toluic acid, terephthalaldehyde (TPA) and 4-carboxybenzaldehyde (4-CBA), as previously quantified [15]. Alcohol was not detected, presumably due to (i) rapid oxidation of alcohols to aldehydes or (ii) esterification of alcohols with acetic acid. A sequence of oxidation process is shown below.



3.1. Low bromide conditions

We have recently published the effectiveness of the Co(OAc)₂/Mn(OAc)₂/NaBr catalyst in the presence of acid additives for pX oxidation. Most reactions were demonstrated with 15 mmol L⁻¹ NaBr and the ratio of total metal ions to bromide ion was 1:1. In an attempt to lower the amount of bromide ion in the catalyst package, a preliminary reaction was carried out with 100 mmol L⁻¹ pX, 10 mmol L⁻¹ Co(OAc)₂ and 10 mmol L⁻¹ Mn(OAc)₂ in HOAc at 70 °C, and then 2.85 mmol L⁻¹ bromide was added to initiate the reaction. Note that 2.85 mmol L⁻¹ bromide corresponds to 81% less bromide than that of our previous studies [15]. The change in the volume of O₂ consumption as a function of time is shown in Fig. 1. No significant O₂ uptake was noted in the absence of bromide ion in first 4000 s. In the presence of 2.85 mmol L⁻¹ bromide, the reaction initiated immediately at an initial rate (*v*_i) of 8.3 × 10⁻⁶ mol L⁻¹ s⁻¹.

The above reaction was further studied in the presences of other additives, e.g. (i) 2.25 mmol L⁻¹ Zr(OAc)₄, (ii) combination of Zr(OAc)₄ and Ce(OAc)₃ and (iii) combination of Zr(OAc)₄ and 5% TFA. A comparison of initial reaction rates for various combinations of additives are summarized in Table 1. These experiments were monitored up to 10–15% of total oxidation as measured by the manometric method.

Comparison of experiments 1–3 reveal that the effect of other metal additives, Zr(OAc)₄ or Ce(OAc)₃, are insignificant in the initial rates determination and little deviation of rates was noted within experimental uncertainty. But, significant improvement in the initial rate was noted in the presence of 5% TFA (experiment #4). The acid additive increased the initial rate by ~11-fold as compare to the one without any acid (experiment #2).

Further experiments were carried out to test the activity of the MC catalyst using 0.28 mmol L⁻¹ NaBr, which amounts to 10 times lower bromide than that used previously and 7–35 times

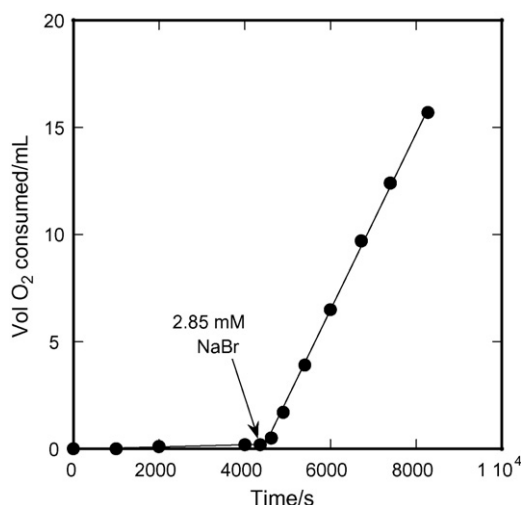


Fig. 1. The volume of O₂ consumed is displayed as a function of time for the autoxidation pX under the following reaction conditions: 10 mmol L⁻¹ Co(OAc)₂, 10 mmol L⁻¹ Mn(OAc)₂, 2.85 mmol L⁻¹ NaBr, and 100 mmol L⁻¹ pX at 70 °C. No bromide ion was present in the first 4000 s. The final volume depicted corresponds to ca. 11% oxidation to TA or 34% to pTAL.

Table 1

Comparison of the initial reaction rates for the autoxidation of pX with the MC catalyst in combination with other additives

Experiment #	Additives	v_i ($\times 10^{-6}$ mol L $^{-1}$ s $^{-1}$)	
		Without Br $^{-}$	2.85 mmol L $^{-1}$ Br $^{-}$
1	–	0.1	8.3
2	2.25 mM Zr(IV)	0.12	11.7
3	2.25 mM Zr(IV) + 10 mM Ce(III)	0.12	9.5
4	2.25 mM Zr(IV) + 5% TFA	0.8	130

Other reaction conditions: 10 mmol L $^{-1}$ Co(OAc) $_2$, 10 mmol L $^{-1}$ Mn(OAc) $_2$, and 100 mmol L $^{-1}$ pX at 70 °C.

lower than the amount of bromide typically used in the MC catalyst for the industrial production of terephthalic acid. Under comparable reaction conditions of 10 mmol L $^{-1}$ Co(OAc) $_2$, 10 mmol L $^{-1}$ Mn(OAc) $_2$, 5 wt% TFA and 100 mmol L $^{-1}$ pX in HOAC at 70 °C, the oxidation proceeded rapidly at the beginning. The initial reaction rate, v_i , was 60×10^{-6} mol L $^{-1}$ s $^{-1}$. But the reaction stopped after consuming only 20 mL of O $_2$ (14% of total O $_2$ required for complete oxidation to terephthalic acid). Further addition of 0.28 mM bromide immediately restarted the reaction with a similar initial rate, but it stopped again after consuming another 20–25 mL of O $_2$. It was also noticed that as the reaction stopped as the solution took on a light brown color, an indication of the accumulation of Mn(III) species, as confirmed by independent experimentation with manganese solutions. The brown coloration disappeared immediately after another addition of bromide and the solution returned to the pink color of the starting Co(II) species. The result is shown in Fig. 2.

3.2. Bromophilic agents

As demonstrated above, cessation of the reaction after 15–20% may be due to the loss of bromide ion in the presence of TFA, where the metal trifluoroacetates formed can rapidly oxidize Br $^{-}$ to Br $_2$. It has been reported in the literature that during the oxidation process, as much as 99% of

the initial bromide is converted to benzylic bromides (4-methyl benzyl bromide and 4-carboxyl benzyl bromide) [9,17,18]. Whereas, inorganic bromide salts are active, covalently bound benzylic bromides are catalytically inactive because of their solvolysis to inorganic bromide is slow [19]. Thus, the concentration of free Br $^{-}$ gradually decreases as the fast radical chain reactions progress. Consequently the reaction suffers from lack of Br $^{-}$, and O $_2$ uptake gradually slows down and finally stops. Therefore, we designed an experiment in the presence of a bromophilic agent, which could bind with Br $^{-}$ to minimize its loss in the formation of benzylic bromides. Zn(OAc) $_2$ is known to be a potential bromophilic agent with binding constant (K_2) of ZnBr $_2$ formation is 2041 L mol $^{-1}$ [20]. An experiment was carried out in the presence of 1.0 mmol L $^{-1}$ Zn(OAc) $_2$, and under comparable conditions of Co(OAc) $_2$ (10 mmol L $^{-1}$), Mn(OAc) $_2$ (10 mmol L $^{-1}$), bromide (0.28 mmol L $^{-1}$), TFA (5 wt%) and pX (100 mmol L $^{-1}$) in HOAC at 70 °C. The beneficial effect of the Zn(OAc) $_2$ was immediately realized; O $_2$ uptake continued even after 50% of total oxidation, as compared to only 14% reaction without Zn(OAc) $_2$. The results are compared in Fig. 3.

The effect of Zn(OAc) $_2$ was further examined by carrying out more experiments at variable concentrations of Zn(OAc) $_2$, in the range of 0.23–10.0 mmol L $^{-1}$, with fixed concentrations of

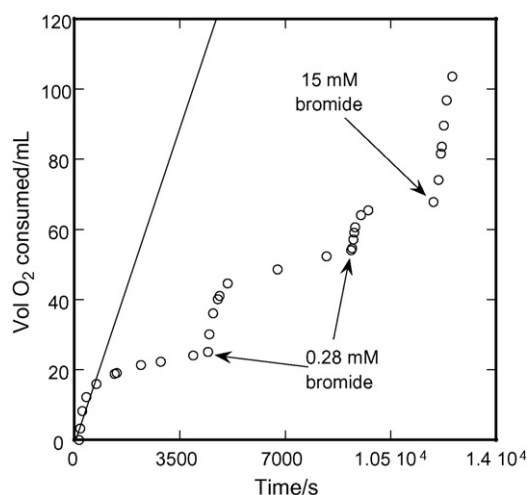


Fig. 2. Volume of O $_2$ consumed as a function of time for the autoxidation of pX with 10 mmol L $^{-1}$ Co(OAc) $_2$, 10 mmol L $^{-1}$ Mn(OAc) $_2$, 0.28 mmol L $^{-1}$ NaBr, 5 wt% TFA and 100 mmol L $^{-1}$ pX in HOAC at 70 °C. Additional bromide was added at each halt.

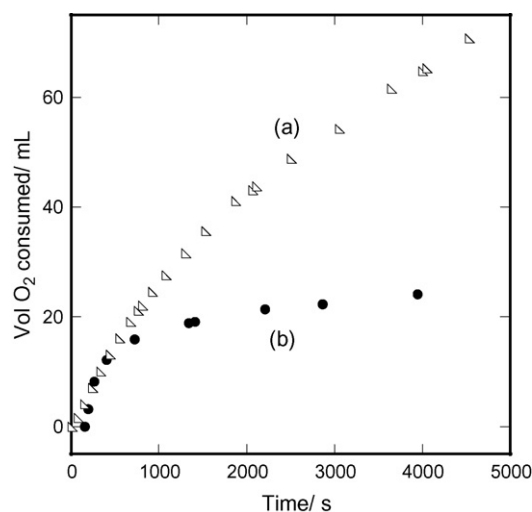


Fig. 3. Volume of O $_2$ consumed as a function of time for the autoxidation of pX (a) with 1.0 mM Zn(OAc) $_2$ and (b) without Zn(OAc) $_2$. Other reaction conditions: 10 mmol L $^{-1}$ Co(OAc) $_2$, 10 mmol L $^{-1}$ Mn(OAc) $_2$, 0.28 mmol L $^{-1}$ bromide, 5 wt% TFA and 100 mmol L $^{-1}$ Co(OAc) $_2$, 10 mmol L $^{-1}$ Mn(OAc) $_2$, 0.28 mmol L $^{-1}$ bromide, 5 wt% TFA and 100 mmol L $^{-1}$ pX in HOAC at 70 °C.

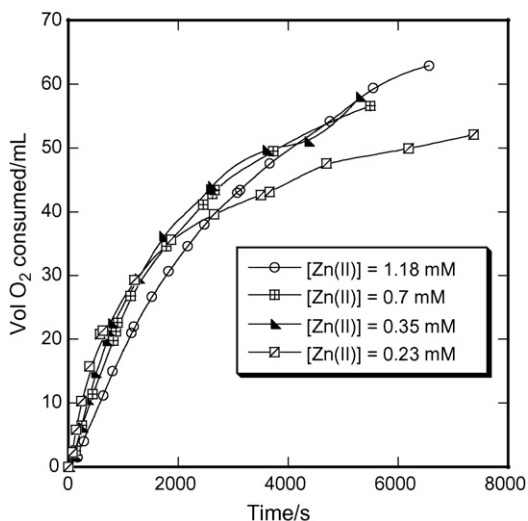


Fig. 4. Volume of O_2 consumed as a function of time for the autoxidation pX at variable concentrations of $Zn(OAc)_2$ under the following reaction conditions: $10 \text{ mmol L}^{-1} \text{ Co(OAc)}_2$, $10 \text{ mmol L}^{-1} \text{ Mn(OAc)}_2$, $0.28 \text{ mmol L}^{-1} \text{ NaBr}$, $0.23\text{--}1.18 \text{ mmol L}^{-1} \text{ Zn(OAc)}_2$, 5 wt\% HFBA and $100 \text{ mmol L}^{-1} \text{ pX}$ at 70°C .

Co(OAc)_2 (10 mmol L^{-1}), Mn(OAc)_2 (10 mmol L^{-1}), bromide (0.28 mmol L^{-1}) and pX (100 mmol L^{-1}). But, 5% heptafluorobutyric acid was used as a source of acid additive, in place of TFA. It has been reported in our earlier publication that the boiling point of HFBA (120°C) is higher than that of TFA (70°C) [15]. Therefore, the loss of HFBA during industrial process of pX oxidation, which usually takes place at $180\text{--}200^\circ \text{C}$, would be minimal. O_2 uptake of each of these reactions was monitored up to $40\text{--}50\%$ of total oxidation (Fig. 4) and the initial reaction rate was determined from the slope. The plot of the initial rates as a function of $Zn(OAc)_2$ concentrations is shown in Fig. 5. It is interesting to note that the initial rates decrease with increase in $Zn(OAc)_2$ concentrations. With a high con-

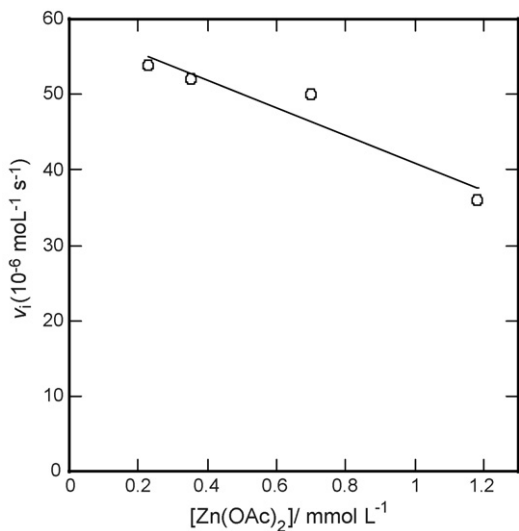


Fig. 5. Plot of the initial reaction rates of the oxidation of pX as a function of $Zn(OAc)_2$. Reaction conditions: $10 \text{ mmol L}^{-1} \text{ Co(OAc)}_2$, $10 \text{ mmol L}^{-1} \text{ Mn(OAc)}_2$, $0.28 \text{ mmol L}^{-1} \text{ NaBr}$, 5 wt\% HFBA , $100 \text{ mmol L}^{-1} \text{ pX}$, and $0.23\text{--}10 \text{ mmol L}^{-1} \text{ Zn(OAc)}_2$ in HO AC at 70°C .

centration of $Zn(OAc)_2$ (10 mmol L^{-1}), the reaction did not initiate in 4000 s . However, too low a concentration of $Zn(OAc)_2$ (0.23 mmol L^{-1}) caused the reaction to cease sooner (Fig. 5).

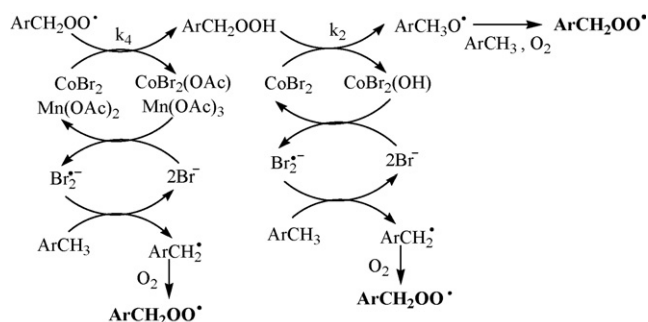
4. Discussion

The free radical chain mechanism of the MC catalyzed autoxidation of methylarenes has been extensively illustrated and published by us and others [14,16,21,22]. Nevertheless, a brief review of the mechanism is useful to facilitate the discussion of beneficial effect of $Zn(OAc)_2$. The chain mechanism is initiated by trace quantity of aralkyl hydroperoxide (ArCH_2COOH), which is inevitably present in pX. ArCH_2COOH reacts with CoBr_2 to generate reactive species, cobalt(III) and aralkoxy radicals ($\text{ArCH}_2\text{O}^\bullet$). In the subsequent step, $\text{ArCH}_2\text{O}^\bullet$ abstracts H-atom from pX (denoted as ArCH_3) to form aralkyl radical (ArCH_2^\bullet), which is then oxygenated to peroxy radical ($\text{ArCH}_2\text{OO}^\bullet$). The peroxy radical reacts with ArCH_3 , Co(II) and Mn(II) to propagate and branch the radical chain reactions. Hence, a single peroxy radical becomes three by a sequence of pathways as shown in Scheme 1.

As shown in Scheme 1, dibromide radicals (HBr_2^\bullet , $\text{Br}_2^{\bullet-}$) are formed in the radical chain mechanism. The role of the dibromide radical is to oxidize ArCH_3 to a carbon-centered radical, ArCH_2^\bullet . However, excess dibromide radical reacts with ArCH_2^\bullet to produce undesired benzylic bromides, in parallel with its desired involvement in the oxidation of ArCH_3 . The reaction between dibromide radical and ArCH_2^\bullet is particularly important when the chain reaction is extremely fast, and consequently, dibromide radical is formed rapidly. Owing to the loss of bromide ion, the catalytic cycles become slower. This effect is particularly alarming when the reaction started with very low amount of bromide. Once fresh bromide ion has been added, the dibromide radical is again generated and the catalytic cycle resumes.

4.1. Role of $Zn(OAc)_2$

It is believed that $Zn(OAc)_2$ reacts with excess bromide ion to form ZnBr^+ (equilibrium constant = 71 L mol^{-1}) [20]. Therefore, the formation of excess bromide radical and its loss to the formation of undesired benzylic bromide is minimized. Importantly, the low equilibrium constant of ZnBr^+ facilitates release



Scheme 1. Chain branching of peroxy radicals in the autoxidation of pX with the $\text{Co(OAc)}_2/\text{Mn(OAc)}_2/\text{Br}^-$ catalyst [21].

of bromide ion as the reaction demands. Thus, the catalytic cycle continues. Of course, Zn does not release bromide from benzylic bromides.

However, exception to the beneficial effect was noted in the presence of high concentration of $\text{Zn}(\text{OAc})_2$ (10 mmol L^{-1}) which did not initiate the oxidation reaction. This exception in the presence of large amount of $\text{Zn}(\text{OAc})_2$ can be explained by higher equilibrium constant of formation of ZnBr_2 (K_2 at 25°C is $21 \times 10^3 \text{ L mol}^{-1}$ in DMSO [20]) than that of CoBr_2 (K_2 at 25°C is 300 L mol^{-1} in HOAc [23]). Thus, the presence of large amount of $\text{Zn}(\text{OAc})_2$ in the reactor favors the formation of ZnBr_2 over to the active catalytic species, CoBr_2 . Consequently the catalytic cycle suffered from lack of both free bromide ion and CoBr_2 , and therefore, the reaction did not initiate.

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