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Photoredox chemistry of mercury ions in aqueous ethanol solutions

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Abstract

Mercury(II) is reduced to mercury(I) upon irradiation (λ_{ir} = 254 nm) in air-saturated aqueous solution containing ethanol. The quantum yield of this reaction linearly depends on the alcohol concentration. The product of this process is Hg_2^{2+}, which is photoactive too. Photostationary state with Hg(I)/Hg(II) ratio depending on the alcohol concentration can be reached in this system. Thus, photoassisted catalytic oxidation of alcohol to aldehyde takes place in such a state. Flash photolysis experiments confirmed that the reactions of Hg^+ and Hg_2^+ formed in the primary steps of the photoinduced process are strongly affected by mercury(II), oxygen, and alcohol. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Mercury ions; Photoredox; Catalytic oxidation; Aqueous ethanol; Intermediates

1. Introduction

Mercury (together with zinc and cadmium) is usually considered as nontransition element because it only forms compounds of full d shell [1,2]. While complexes of divalent mercury generally display strong thermal stability, mercurous compounds tend to disproportionate. Hence, the photochemical behavior of several mercury(II) complexes has extensively been studied in solution [3–5]. The photochemistry of monomeric halo and pseudohalo complexes was characterized by ligand-to-metal charge-transfer (LMCT) behavior both in aqueous [6,7] and in organic [8,9] systems. Similar feature was observed for triazidomercurate(II) [10]. In di- and trinuclear complexes with cobalt and iron, mercury(II) also underwent photoinduced intramolecular reduction due to metal-to-metal charge transfer (MMCT) [11,12].

So far, however, only scant attention has been paid to the photochemistry of inorganic mercury(I) compounds. While photoexcitation (λ_{ir} = 254 nm) of Hg_2^{2+} ion in deaerated, aqueous solution did not cause any permanent chemical change, formation of Hg(II) and H_2O_2 was observed in air-saturated system [13,14]. In contrast, UV photolysis (λ_{ir} = 254 nm) of the dimercury(I) cation in the presence of cyclohexene [15] or alcohol [16] resulted in a reduction to elemental mercury. In the latter case, when this process took place in argon-flushed water–ethanol mixtures containing mercury(II), photocatalytic formation of Hg_2^{2+} was realized. The efficiency of this photocatalytic self-generation proved to be sensitive to the presence of oxygen and to the alcohol content of the solvent.

The aim of this work was to continue the photochemical investigation of the Hg_2^{2+}–Hg^{2+} system in aqueous ethanol solution in order to elucidate the individual roles of the different mercury species in the mechanism of the photoinduced reactions taking place in this catalysis.

2. Experimental

Stock solutions of reagent grade $Hg_2(ClO_4)_2$, $Hg(ClO_4)_2$, and $HClO_4$ were used to prepare the solutions of desired composition for photochemical experiments. Reagent grade ethanol and triply distilled water were applied as solvents. The solutions containing both ethanol and mercury(II) were always freshly prepared, in order to avoid their thermal reaction before the photolysis. Deoxygenation of the samples was carried out by purging argon for at least 1 h before the measurements. Care was taken to avoid ethanol loss during this procedure.

For continuous irradiation at 254 nm, a low pressure mercury arc lamp (16 W, Applied Photophysics) was utilized. Incident light intensity was determined by ferrioxalate actinometry ($I_0 = 2.5 \times 10^{-9}$ mol photon s^{-1}). Quantum yield measurements were carried out with samples of nearly

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100% light absorption. In these experiments the conversion did not exceed 5%. The absorption spectra were recorded using either a GBC 911A or a Specord UV–Vis spectrophotometer, in 5-mm quartz cuvettes. Typically, the irradiations were carried out with 10 cm^3 solutions in 5-cm cells at room temperature.

Time-resolved spectra and transient absorption curves were determined by a laser flash photolysis system previously described [17]. A Brilliant (Quantel) Nd-YAG laser with frequency quadrupling served as light source yielding 266-nm pulses of about 10 ns duration. Samples were irradiated in 1-cm fluorescence cells with right-angle monitoring of the transient absorbance. For processing the transient absorption curves, a MS Excel 97 program was applied. Generally, the signals evaluated were the averages of five individual transients. Aldehyde formed during the photolyses was quantitatively determined by a photometric method, which is based on the transformation to 2,4-phenylhydrazon absorbing at 478 nm [18].

3. Results and discussion

3.1. Photoinduced reduction of Hg^{2+}

In our earlier study of the photocatalytic self-generation of $Hg_2{}^{2+}$ in the presence of Hg^{2+}, the absorbance of the latter species at the irradiation wavelength (254 nm) was negligible compared to that of the dimercury(I) cation at the same concentration (5×10^{-5} M each) [16]. Furthermore, the quantum yields for the photoinduced reaction of $Hg_2{}^{2+}$ were about the same in both the absence and the presence of mercury(II), indicating that the mercury(I) cation is basically responsible for the photoactivity of the system at 254-nm excitation. It could not, however, be excluded that the Hg^{2+} ions are also photosensitive at this irradiation wavelength. In order to check this possibility, air-saturated solutions containing 0.1 M perchloric acid, Hg^{2+} in relatively high concentration (5×10^{-3} M) giving considerable absorbance at 254 nm in 5-cm cuvette and variable amount of alcohol were photolyzed. Irradiation of these solutions led to the formation of $Hg_2{}^{2+}$ indicated by the appearance of the 237-nm absorption band of this species (Fig. 1). The quantum yields (Φ) for the photoinduced reduction of Hg^{2+} were determined from the initial rate of the $Hg_2{}^{2+}$ formation monitored at 237 nm in solutions of different alcohol contents (Fig. 2). As it can be seen in Fig. 2, Φ consistently increases as the alcohol content (v/v) becomes greater. At alcohol concentrations less than 15 % (v/v, i.e, 2.6 M) the quantum yield is lower than the error of the measurement. This suggests that the overall reaction (1) takes place via formation of an intermediate which can also react with oxygen. The most probable candidate for this is Hg^+, which can be formed in the primary photochemical step (reaction (2)).

$$2Hg^{2+} + CH_3CH_2OH \xrightarrow{h\nu} Hg_2^{2+} + CH_3CHO + 2H^+ \qquad (1)$$

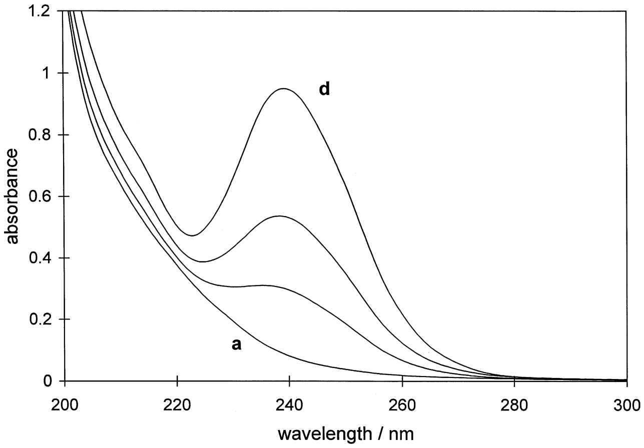

Fig. 1. Temporal spectral changes during the photolysis of 4.5×10^{-5} M $Hg(ClO_4)_2$ in air-saturated ethanolic solution containing 10% (v/v) H_2O and 0.1 M $HClO_4$. Curves a and d are for 0 and 70-min irradiation time ($\lambda_{ir} = 254$ nm).

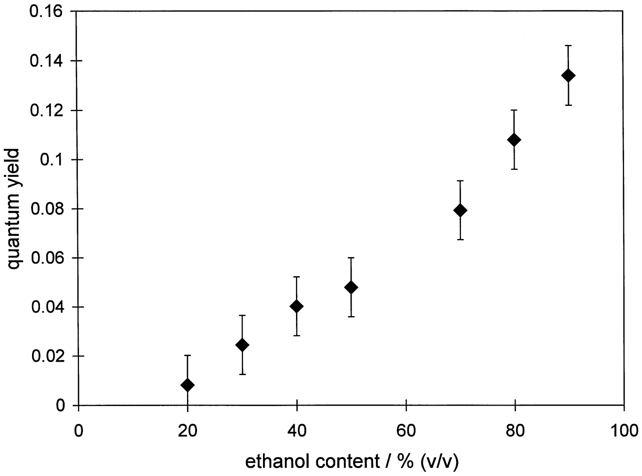

Fig. 2. Quantum yield vs alcohol content for the photoreduction of Hg^{2+} in EtOH–H_2O mixture ($\lambda_{ir} = 254$ nm, 4.5×10^{-5} M $Hg(ClO_4)_2$, 0.1 M $HClO_4$).

$$Hg^{2+} + CH_3CH_2OH \xrightarrow{h\nu} Hg^+ + CH_3CHOH + H^+ \qquad (2)$$

In pulse radiolysis experiments with Hg^{2+}, this species was observed as the first intermediate formed after electron scavenging by mercury(II) [19–21].

In air-saturated solution both ethanol and oxygen can compete for this intermediate. The rate constant for the latter reaction is rather high (≈10^9 M^{-1}s^{-1}) [22] indicating that for an efficient reductive scavenging a considerable alcohol concentration is required. This was also confirmed by our observations; while in oxygen-free (argon-saturated) system photoreduction of Hg^{2+} could be realized at alcohol content as low as 0.03 M, in aerated solution 2.6 M ethanol was needed for the same result.

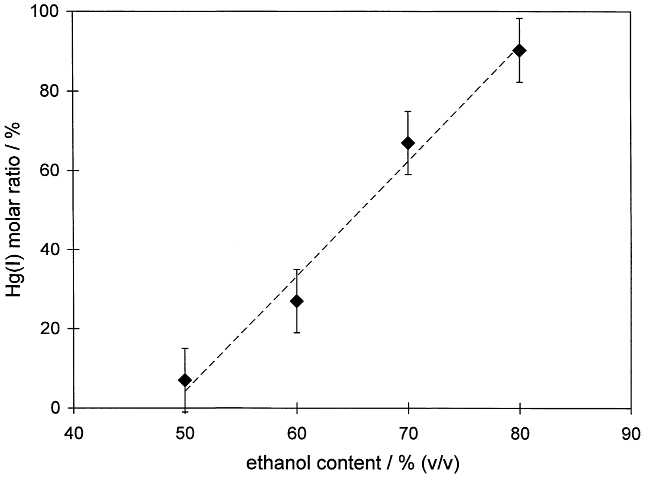

Fig. 3. Molar ratio of Hg(I) in the photostationary state as a function of alcohol content in air-saturated EtOH–H_2O mixture containing 4.5×10^{-5} M mercury (λ_{ir} = 254 nm, 0.1 M $HClO_4$).

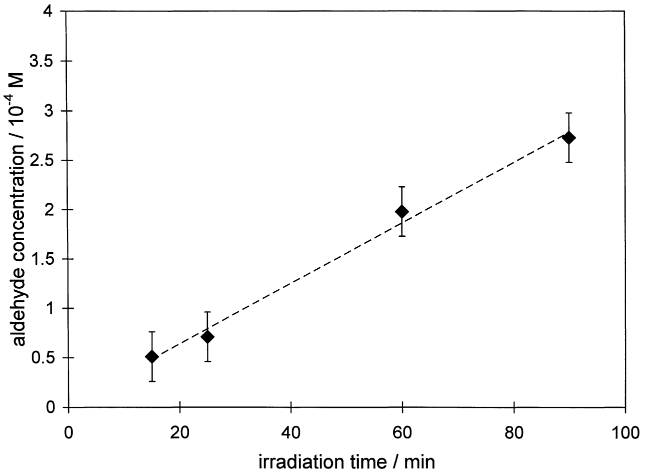

Fig. 4. Formation of aldehyde as a function of irradiation time in air-saturated 70% (v/v) EtOH–H_2O mixture containing 3×10^{-5} M $Hg_2(ClO_4)_2$ and 3×10^{-5} M $Hg(ClO_4)_2$ (λ_{ir} = 254 nm, 0.1 M $HClO_4$).

3.2. Photoassisted catalytic oxidation of alcohol

When photolysis of air-saturated acidic (0.1 M $HClO_4$) Hg^{2+} solution containing alcohol (70% v/v) was made for extended periods of time, after a while the formation of $Hg_2{}^{2+}$ was stopped and the $Hg_2{}^{2+}/Hg^{2+}$ concentration ratio remained constant upon further irradiation. This photostationary state was determined by the alcohol content of the solution (at constant total mercury concentration, 4.5×10^{-5} M Hg(II), and constant light intensity), the higher the alcohol concentration, the larger this ratio (Fig. 3). The photolysis of an $Hg_2{}^{2+}$ solution (C = 2.25×10^{-5} M, i.e, with the same total mercury concentration) of the same acid and given alcohol concentration resulted in the oxidation of the dimercury(I) cation. However, as in the previous case, after a certain period of time a constant $Hg_2{}^{2+}/Hg^{2+}$ concentration ratio was reached in the photolyzed solution and it did not change during further irradiation. This ratio was equal to the value measured in the photolyzed solution of the same alcohol content. It means that in acidic (0.1 M $HClO_4$) solution, at a given total mercury concentration (and constant light intensity), the alcohol content of the system determines the $Hg_2{}^{2+}/Hg^{2+}$ ratio after the photostationary state has been reached.

In the photostationary state most of the light (at 254-nm irradiation) is absorbed by the $Hg_2{}^{2+}$ species. Its primary photochemical reaction also leads to the formation of Hg^+ as it was suggested earlier [14–16] and has been proved quite recently [23].

$$Hg_2{}^{2+} \xrightarrow{h\nu} 2Hg^+ \tag{3}$$

One may conclude that in the photostationary state the rate of the oxidation of this species with oxygen is equal to that of its reduction with alcohol. However, the rate of these reactions of Hg^+ can be different even in the photostationary state because the efficiency of the overall oxidation and reduction processes are influenced by the subsequent thermal reactions. The counterpoised effect results in no change in the $Hg_2{}^{2+}/Hg^{2+}$ ratio.

Although the concentration of the $Hg_2{}^{2+}$ and Hg^{2+} species are constant in the photostationary state, there is a net reaction taking place in this system, namely the oxidation of alcohol to aldehyde. In order to demonstrate this photoassisted catalytic oxidation of EtOH, solutions of 0.1 M $HClO_4$, 70% (v/v) EtOH, 3×10^{-5} M Hg^{2+} and 3×10^{-5} M $Hg_2{}^{2+}$ (this $Hg_2{}^{2+}/Hg^{2+}$ ratio corresponds to the photostationary state at the given alcohol content) were irradiated for various time intervals. After the photolyses, the aldehyde formed was determined in each solution. As it can be seen in Fig. 4, the aldehyde concentration proportionally increased with the irradiation time (while the $Hg_2{}^{2+}/Hg^{2+}$ ratio remained constant). Fom the slope of this function, 0.06 was determined to be the quantum yield for the formation of aldehyde in this system. This value is in accordance with the quantum yields for the photoinduced reduction of $Hg_2{}^{2+}$ [16] and for the formation of Hg^+ from $Hg_2{}^{2+}$ [23]. These results confirmed that in the photostationary state a photoassisted catalytic oxidation takes place. No detailed product analysis was carried out, but in a similar system (Cu(II)/EtOH/H_2SO_4) photocatalytic oxidation of alcohol gave acetaldehyde as the main product and negligible amount of acetic acid [24]. Formation of mercurated compounds can be neglected here because the concentration of the mercury ions did not change during the photolysis.

3.3. Flash photolysis of $Hg_2{}^{2+}$

Both in the photoinduced reduction of Hg^{2+} with alcohol and upon excitation of $Hg_2{}^{2+}$, the formation of Hg^+ has been suggested to occur in the primary photochemical steps. The negligible absorbance of Hg^{2+} at 266 nm excluded its excitation with our laser system, however, $Hg_2{}^{2+}$ could be studied by flash photolysis. Excitation of deaerated solution

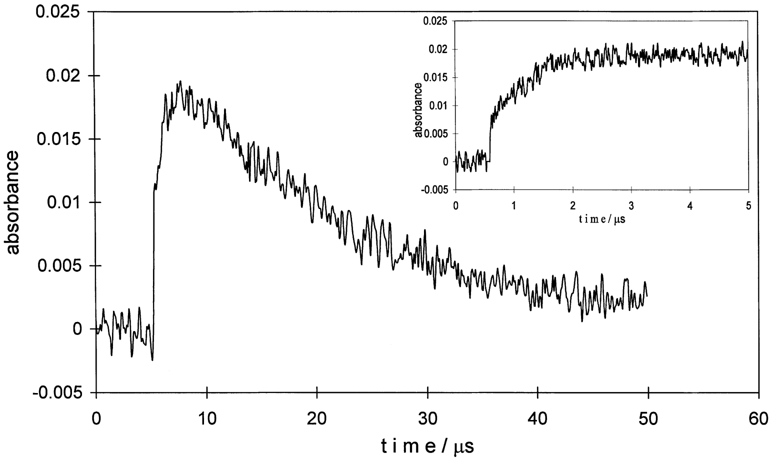

Fig. 5. Transient absorption trace at 285 nm in aqueous solution of $Hg_2{}^{2+}$ (1×10^{-3} M $Hg_2(ClO_4)_2$, 0.1 M $HClO_4$) flashed with 266-nm laser pulse (time delay 5 μs). Inset: the buildup of the absorption signal recorded at 10 times higher time resolution (time delay 500 ns).

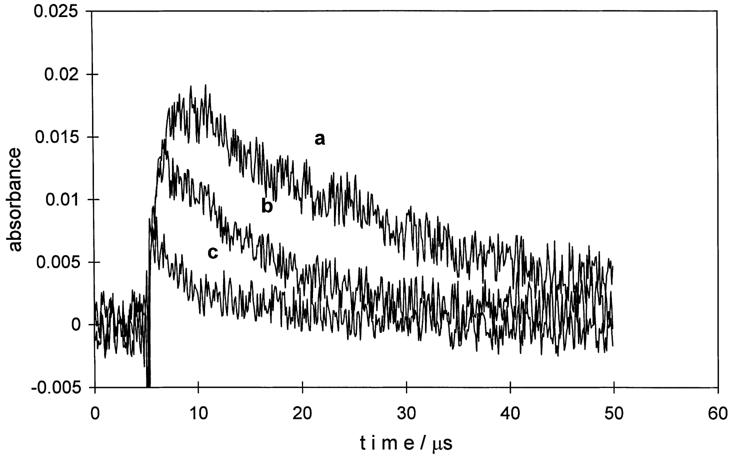

Fig. 6. Transient absorption traces at 285 nm in aqueous solution of $Hg_2{}^{2+}$ (1×10^{-3} M $Hg_2(ClO_4)_2$, 0.1 M $HClO_4$) in the presence of (a) 0, (b) 3.3×10^{-4}, and (c) 2×10^{-3} M Hg^{2+} , flashed with 266-nm laser pulse (time delay 5 μs).

of 1×10^{-3} M $Hg_2{}^{2+}$ with a 266-nm pulse resulted in the formation and decay of at least two intermediates. The transient absorption curve recorded at 285 nm indicated the appearance of a species right after the pulse (Fig. 5, inset). Subsequently, the buildup and decay of a longer-lived intermediate can be observed over a longer time scale. The transient spectra belonging to the initial (right after the pulse) and the maximum (3 μs after the pulse) absorbances were unambiguously assigned to Hg^+ and $Hg_2{}^+$, respectively [23]. The previous species is formed in the primary photochemical step (reaction (3)). Its subsequent reaction (4) with Hg^0 produces $Hg_2{}^+$.

$$Hg^+ + Hg^0 \rightarrow Hg_2{}^+ \quad (4)$$

Elemental mercury can exist in the system from the disproportionation of $Hg_2{}^{2+}$.

$$Hg_2{}^{2+} \Leftrightarrow Hg^0 + Hg^{2+} \quad (5)$$

The important role of reactions (4) and (5) is confirmed by the effect of the Hg^{2+} concentration on the formation of $Hg_2{}^+$. Increasing the concentration of mercury(II) in the system reduces both the buildup rate of $Hg_2{}^+$ and its maximum amount formed after the pulse. Besides, as it is shown in Fig. 6, the decay rate of this intermediate is significantly enhanced upon addition of Hg^{2+}. It suggests that the latter phenomenon may be interpreted by reaction (6).

$$Hg_2{}^+ + Hg^{2+} \rightarrow Hg_2{}^{2+} + Hg^+ \quad (6)$$

Both $Hg_2{}^+$ and Hg^+ can undergo recombination too (reactions (7) and (8)).

$$Hg_2{}^+ + Hg_2{}^+ \rightarrow Hg_2{}^{2+} + 2Hg^0 \quad (7)$$

$$Hg^+ + Hg^+ \rightarrow Hg_2{}^{2+} \quad (8)$$

At the actual concentrations, however, these processes are about one order of magnitude slower than reactions (4) [23,25] and (6) [26].

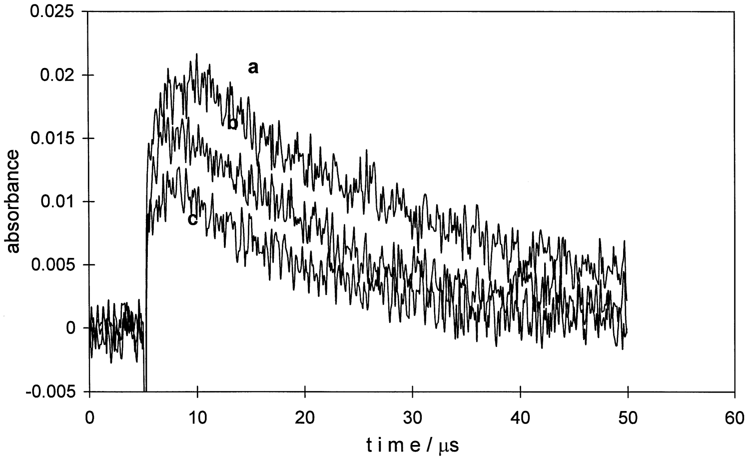

Fig. 7. Transient absorption traces at 285 nm in aqueous solution of Hg_2^{2+} (1×10^{-3} M $Hg_2(ClO_4)_2$, 0.1 M $HClO_4$) in the presence of (a) 1, (b) 3, and (c) 5 M EtOH, flashed with 266-nm laser pulse (time delay 5 μs).

The results of flash photolysis experiments with air-saturated solutions were similar to those experienced upon addition of Hg^{2+}. It is the consequence of the reactions (9) and (10) of Hg^+ and Hg_2^+ with oxygen [25,26].

$$Hg^+ + O_2 \rightarrow Hg^{2+} + O_2^- \quad (9)$$

$$Hg_2^+ + O_2 \rightarrow Hg_2^{2+} + O_2^- \quad (10)$$

Since the quantum yield of the photoinduced reduction of Hg_2^{2+} in this system strongly depends on the ethanol content, the effect of the EtOH concentration on the formation and decay of Hg_2^+ may also serve some information regarding the mechanism of the photoinduced processes. The transient absorption curves in Fig. 7 clearly indicates that increasing the ethanol concentration decreases the maximum concentration of Hg_2^+. Since the decay rate of this species proved to independent of the ethanol content, a reaction (11) of Hg^+ competing with reaction (4) resulted in this phenomenon.

$$Hg^+ + CH_3CH_2OH \rightarrow Hg^0 + CH_3CHOH + H^+ \quad (11)$$

Thus, reaction (11) is the key step in the photocatalytic oxidation of ethanol in this system. The organic radical can also react with oxygen, giving aldehyde as a final product. In accordance with the results of the CW experiments, rather high alcohol concentrations were needed for appreciable effects on the formation of Hg^+. This suggests that the rate constant of reaction (11) must be several orders of magnitude lower than that of reaction (4).

4. Conclusion

Both Hg^{2+} and Hg_2^{2+} ions undergo reduction upon irradiation ($\lambda_{ir} = 254$ nm) in aqueous ethanol solution. In air-saturated solution, photostationary state with Hg(I)/Hg(II) ratio depending on the alcohol concentration can be reached. Photoassisted catalytic oxidation of alcohol to aldehyde takes place in such a state. The primary photochemical steps in this system (reactions (2) and (3)) produce the Hg^+ intermediate, which can undergo both oxidation and reduction in the presence of oxygen and ethanol, respectively. The latter reaction is the key step in the photocatalytic oxidation of alcohol. Besides, Hg^+ can also be transformed to the longer-lived Hg_2^+ intermediate in another competitive reaction.

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