

Chlorinated byproducts from the photoassisted catalytic oxidation of trichloroethylene and tetrachloroethylene in the gas phase using porous TiO₂ pellets

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Abstract

The photocatalytic degradation of trichloroethylene and tetrachloroethylene in the gas phase, when porous TiO₂ pellets were used, produced such undesirable chlorinated byproducts as chloroform (CHCl₃) and carbon tetrachloride (CCl₄). The formation of byproducts was reduced by increasing oxygen mole fractions in the feed gas stream and/or using the TiO₂ pellets fired at a lower temperature. Theoretical calculations indicate that the Cl-radical-initiated reaction produces these byproducts. On the basis of the experimental and the theoretical results, a method to prevent the formation of the chlorinated byproducts is discussed.

Keywords: Photocatalytic degradation; Trichloroethylene; Tetrachloroethylene

1. Introduction

Many cases have been reported of the contamination of soil and groundwater supplies owing to such volatile organic compounds (VOCs) as trichloroethylene (TCE) and tetrachloroethylene (PCE) [1]. Heterogeneous photocatalysis using TiO₂ particles is pregnant with great promise as a simple and inexpensive method to mineralize these contaminants [2]. We previously reported the results of TCE photodegradation using TiO₂ pellets prepared by sol-gel techniques [3], where TCE was completely degraded to CO₂ and HCl at 64 °C when monochloroacetic acid was formed as the primary product at 23 °C [4].

The combination of a soil vapor extraction (SVE) unit and a gas phase reactor with TiO₂ can be applied to the practical decontamination of VOCs in the environment. Annular photoreactors packed with the TiO₂ pellets were field tested for 5 days at Savannah River Site in Aiken, SC. When the reactor was used to treat 222–1100 vol.ppm TCE and 1900–7000 vol.ppm PCE contained in the effluents from an SVE unit, no appreciable TCE and PCE were observed in the outlet gas stream, i.e. 100% conversion was achieved. However, carbon tetrachloride and chloroform were detected as the minor byproducts [5]. To make special mention of the former chloro compound, it is carcinogenic and reported to be one

of the chemicals difficult to degrade by TiO₂-mediated photocatalytic oxidation [6]. Therefore, for the practical use of this technology, it is a necessity to find operating conditions which do not produce such undesirable byproducts.

In the present study, first, the effect of reaction conditions on the formation of byproducts will be described. Second, on the basis of the experimental results, a discussion will be given about the reaction mechanisms that form CHCl₃ and CCl₄, the mechanisms suggested by the results of ab initio molecular orbital (MO) calculations. This is a very viable method in investigating the reaction mechanism in which monochloroacetic acid is formed by the attack of the OH radical at the TCE molecule [7]. Last of all, a method which prevents the chlorinated byproducts from forming in the reactor will be discussed.

2. Experimental details

The photodegradation experiments were carried out in a packed bed tubular photoreactor in a non-circulating mode, with a set of four 4 W fluorescence black light bulbs (GE F4T5-BLB) surrounding the tubular reactor. TiO₂ pellets (1 mm in diameter) were prepared by the sol-gel method and fired at 200–550 °C [3]. The gas stream was heated at a

desired temperature with heating tapes (Thermolyne) and the temperature controller (Glas Col PL 312). The concentrations of CHCl_3 and CCl_4 were analyzed by gas chromatography (Hewlett-Packard 5890) with a thermal conductivity detector (TCD). The apparatus and analytical method have been previously described [3,4].

The ab initio MO calculations were performed using the GAUSSIAN86 program [8] at the Institute for Molecular Science and the GAUSSIAN92 program for the Fujitsu S4/10 (SUN SPARCstation 10) computer [9]. We used the 6-31G basis set [10] for geometry optimization of all the molecules investigated here. For the sake of a better energy description, we performed MP2/6-31G**/HF/6-31G calculations.

3. Results and discussion

3.1. Photodegradation experiments

When a gas stream containing 450 vol.ppm TCE, 2×10^4 vol.ppm O_2 and 6000 vol.ppm H_2O passed through 0.42 g TiO_2 pellets at 50 ml min^{-1} , 67.5°C , no trace of TCE was detected in the outlet gas, i.e. 100% degradation was achieved. The stoichiometry ratio $\gamma_{\text{CO}_2:\text{TCE}}$ of $[\text{CO}_2]_{\text{produced}}/[\text{TCE}]_{\text{degraded}}$ was 1.7 after 30 min of irradiation. $[\text{CO}_2]_{\text{produced}}$ and $[\text{TCE}]_{\text{degraded}}$ indicate the concentrations of the produced CO_2 and the degraded TCE respectively. The ratio increased gradually as irradiation time increased, remaining at the then highest ratio for ca. 2 for 3 days. It took 16 h to heat the pellets until the desired temperature was reached. After a steady state had been attained, a small chromatographic peak was observed to be assigned to CHCl_3 during the experiments. The amount of CHCl_3 was less than 10 vol.ppm in the outlet gas stream. This finding agrees with the value of ca. 2 for $\gamma_{\text{CO}_2:\text{TCE}}$ obtained by the experiments.

Fig. 1 shows the relations between the TCD peak height for CHCl_3 and the firing temperature of TiO_2 pellets. Under the experimental conditions employed, 100% TCE conversion was achieved for these pellets. The peak of CHCl_3 completely disappeared when the TiO_2 pellets were fired at 200°C . TiO_2 fired at higher than 300°C produced CHCl_3 , whose amount increased almost in proportion to the firing temperature.

Both porosity and specific surface area of the pellets decreased as the firing temperature increased as shown in Fig. 2. The TiO_2 pellets fired at 500°C have a porosity of 38% and a specific surface area of $44 \text{ m}^2 \text{ g}^{-1}$ while at 300°C they are 55% and $189 \text{ m}^2 \text{ g}^{-1}$ respectively. The catalyst in the former firing produced four times as much CHCl_3 as that in the latter. Thus, it follows that the surface area and the porosity are closely related to the formation of byproducts.

The O_2 mole fraction also changes the amount of CHCl_3 in the outlet gas stream as shown in Fig. 3. With the increase in the amount of O_2 , the TCD signal height plunged, until the formation of CHCl_3 was completely suppressed at 2×10^5 vol.ppm O_2 in the inlet gas. It also follows that the large

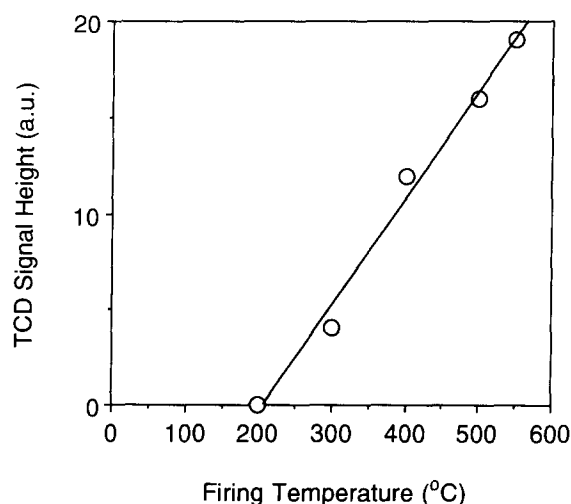


Fig. 1. The relation between the peak height of TCD for CHCl_3 and the firing temperature of TiO_2 pellets. The gas stream, containing 450 vol.ppm TCE, 2×10^4 vol.ppm O_2 , and 3×10^3 vol.ppm water vapor, passed through 0.42 g TiO_2 at 26 ml min^{-1} at 67.5°C . 1 arbitrary unit (a.u.) on the ordinate corresponds to 0.3–0.4 vol.ppm in concentration.

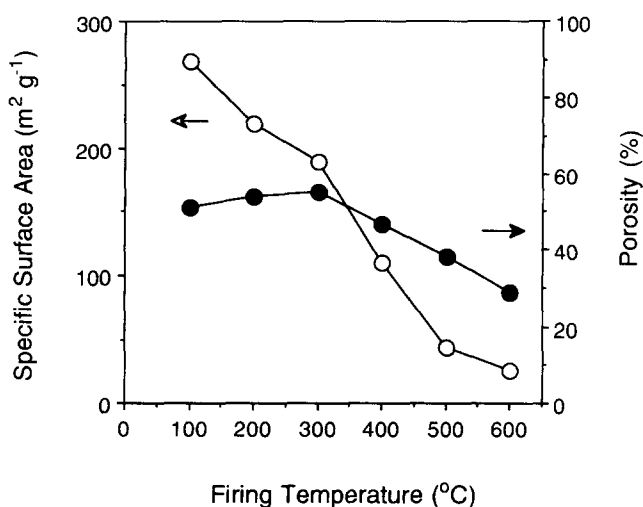


Fig. 2. The dependence of specific surface area and porosity of the TiO_2 pellets on the firing temperature.

surface area, the high porosity and the high amount of O_2 in the feed gas stream are the key factors in avoiding the formation of CHCl_3 .

When PCE degradation experiments were performed at 67.5°C under various conditions such as 250–450 vol.ppm PCE, $(3\text{--}9) \times 10^3$ vol.ppm H_2O , $(6\text{--}20) \times 10^4$ vol.ppm O_2 and space times of $(4.0\text{--}10.8) \times 10^7 \text{ g s mol}^{-1}$, no PCE was detected in the outlet gas; hence 100% conversion took place. In this case, a small peak was observed and assigned to CCl_4 . For PCE photodegradation the TiO_2 pellets were also used, fired at several different temperatures. The pellets fired at a lower temperature produced less CCl_4 in the outlet gas stream: at 200°C , they completely suppressed the generation of CHCl_3 from TCE with only 10–20 vol.ppm CCl_4 as a product. A higher mole fraction of O_2 is also effective in suppressing the formation of CCl_4 as shown in Fig. 3.

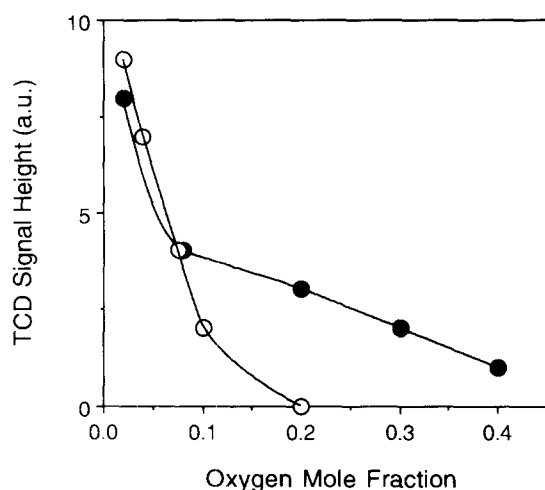


Fig. 3. Effect of the O_2 mole fraction in the feed gas stream on the concentration of $CHCl_3$ (O) formed from TCE or CCl_4 (●) from PCE photodegradation. The gas stream containing 400 vol.ppm TCE passed through TiO_2 fired at $400^\circ C$ at 26.1 ml min^{-1} or containing 300 vol.ppm PCE passed through TiO_2 fired at $200^\circ C$ at 50 ml min^{-1} . The other conditions are the same as for Fig. 1.

Although the precise concentration of CCl_4 in the outlet gas is difficult to estimate, at least twice as much CCl_4 was produced from PCE as $CHCl_3$ from TCE for a gas stream containing 450 vol.ppm PCE or TCE, 2×10^4 vol.ppm O_2 and 3×10^3 vol.ppm H_2O , passed through 0.42 g TiO_2 pellets at 26 ml min^{-1} , $67.5^\circ C$.

3.2. Cl-radical-initiated reaction mechanism

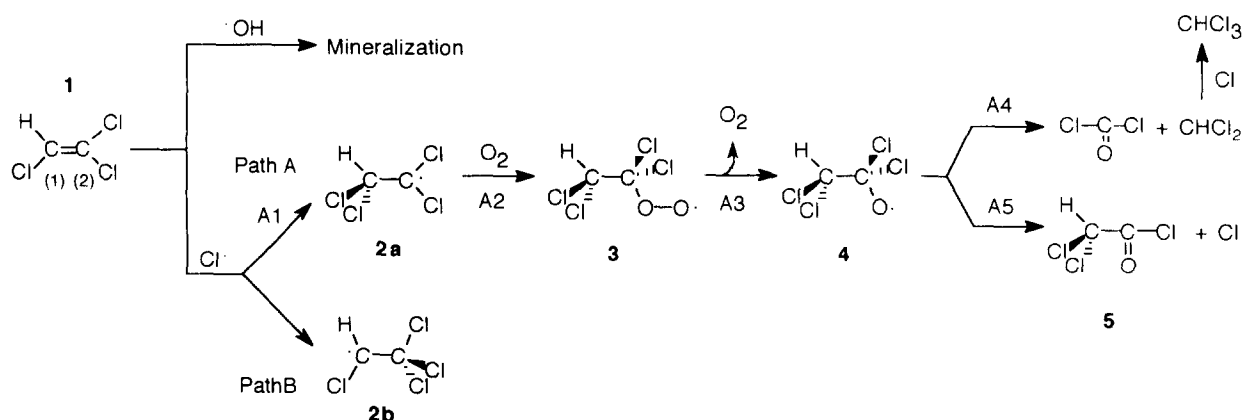
In the TiO_2 -mediated photodegradation, OH radicals are major reactive species for the oxidation of organic substrates. We have clarified the photodegradation mechanism of TCE initiated by the OH radical [7]. Kirchner et al. [11] reported the results of the degradation of TCE **1** with the OH radical in the gas phase. In order to explain the formation of C_2HCl_4 , they proposed, as shown in Scheme 1, the initial formation of Cl radicals and the subsequent preferential attack at the $CHCl$ side (path A1). Sanhueza et al. [12] found that the

Cl-radical-initiated oxidation of TCE produces dichloroacetyl chloride and phosgene. In their experiments, Cl_2 was photolyzed in the presence of chlorinated ethylenes. Nimlos et al. [13], who detected the reaction products reported by Sanhueza et al., indicated that the Cl-radical-initiated reaction plays a significant role in photocatalytically oxidizing TCE on TiO_2 . In their reaction scheme, the Cl radicals come from the intermediates when TCE reacts with the OH radical.

The Cl-radical-initiated reaction can yield other products such as $CHCl_3$ and CCl_4 from TCE and PCE photodegradation respectively. Hence, the explanation for $CHCl_3$ formation is shown in Scheme 1. The addition of the OH radical, abundant on the surface of the TiO_2 [14], to the TCE molecule proved by calculation to be exothermic by $-41.0\text{ kcal mol}^{-1}$ [7], and so did the Cl addition, but only by $-14.7\text{ kcal mol}^{-1}$. Thus, it can be gathered that the Cl-radical-initiated reaction seldom occurs on the catalyst surface, i.e. in the gas phase the Cl radicals which escape from the surface react with TCE or PCE and form undesirable byproducts.

The Cl radical can attack both C(1) (path A1) and C(2) (path B) of TCE. In a preliminary calculation with the PM3 hamiltonian in the MOPAC version 6 program [15], the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) of TCE were examined to determine the possibility of paths A1 and B: both their HOMOs and their LUMOs are relevant to addition of the Cl radical to TCE [16]. Calculations were carried out for the orbital coefficients of C(1) and C(2): they turned out 0.463 in the HOMO and 0.686 in the LUMO for C(1) whereas, for C(2), they were 0.411 in the HOMO and -0.670 in the LUMO. The fact that MO coefficients in C(1) are larger than in C(2) suggests that the Cl radical preferentially attacks C(1). The stabilization energy for path A1 was calculated to be $-14.7\text{ kcal mol}^{-1}$, whose absolute value is larger by 5.0 kcal mol^{-1} than that for path B. Therefore, we will discuss only path A in further detail.

2a reacts with O_2 , forming peroxy radical **3**, because of the radical center on the carbon atom in **2a** (path A2) [17], which is easily understood; **3** in turn dimerizes, decomposing into two oxyl radicals **4** and O_2 (path A3); finally, the cleavage of the C–C bond in **4** leads to the formation of phosgene



Scheme 1.

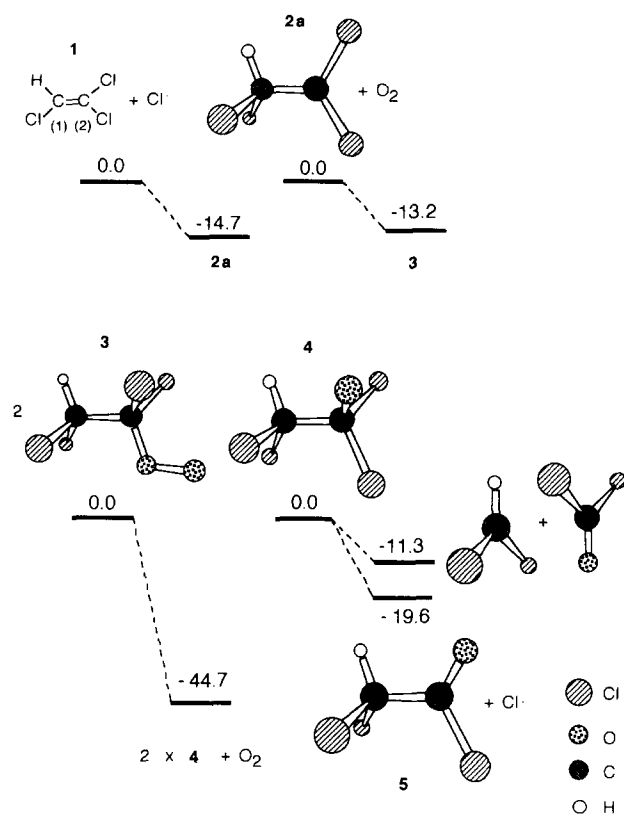


Fig. 4. Optimized structures and energy level diagram of TCE photodegradation initiated by the Cl[·] attack to the CHCl side of the TCE molecule (path A). All the energies were estimated with MP2/6-31G**/HF/6-31G calculations. For path A2, we used the energy of the triplet oxygen molecule.

and CHCl₂ radical (path A4) on the one hand, and, on the other, 4 releases a Cl radical, forming a dichloroacetyl chloride 5 (path A5). In Fig. 4 these reactions are represented in terms of energy levels, wherein path A5 is exothermic by $-19.6 \text{ kcal mol}^{-1}$. After 5 is adsorbed onto the TiO₂ surface, this molecule further reacts with H₂O adsorbed onto the surface and/or into the pores of the TiO₂ pellets:



According to Kraeutler and Bard [18], who proposed the formation of CH₃ radical from acetic acid, decarboxylation of dichloroacetic acid, in theory, produces a CHCl₂ radical, resulting in the formation of CHCl₃. However, inasmuch as the trace of CHCl₃ was all that our system observed, the dichloroacetic acid was degraded to CO₂ and HCl at 67.5 °C, at which temperature monochloroacetic acid, instead of accumulating, was degraded to CO₂ and HCl on the TiO₂ surface.

The energy differences between paths A4 and A5 is so small, in fact as small as $8.3 \text{ kcal mol}^{-1}$, that path A4 can also be considered to be the decomposition mechanism of 4. The formation of a CHCl₂ radical accompanies production of phosgene, which is one of the products observed on the TiO₂ catalyst [13]. No appreciable phosgene was detected even in the high concentration of TCE and PCE contaminating the gas stream in our system [5]. It is well known that phosgene reacts with H₂O and forms CO₂ and HCl [19].

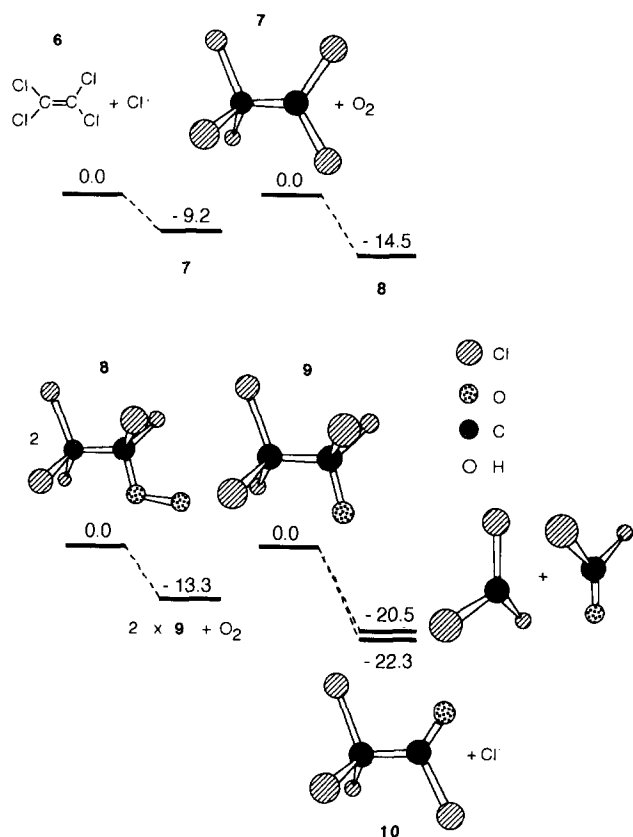


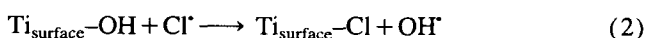
Fig. 5. Optimized structures and energy level diagram of PCE photodegradation by Cl radical.

Water molecules adsorbed onto the TiO₂ surface or trapped in pores also play a significant role in decomposing phosgene into HCl and CO₂.

A similar reaction is also conceivable for PCE 6. The energy diagram of the reaction is represented in Fig. 5, where the radical intermediate 7 is converted to 9 via reaction paths similar to path A2 and A3 for TCE, and the C–C bond cleavage of 9 produces a CCl₃ radical, which in turn reacts with a Cl radical forming CCl₄. The chloro compounds were observed in the PCE photodegradation.

3.3. Suppression of the formation of byproducts

According to the results from both experiments and theoretical calculations in the present study, it is possible to work out a strategy for suppressing the formation of the undesirable byproducts under consideration, the strategy being that, if the Cl radicals are trapped on the TiO₂ surface or eaten up by the molecules in the inlet gas, the byproducts will not be produced via the Cl-radical-initiated mechanism. The Cl radical produced are adsorbed onto or trapped on the catalyst surface. The photoelectron in the conduction bands of TiO₂ reduces the Cl radical to a Cl⁻ anion, which is adsorbed onto the TiO₂ surface [20]. Boonstra and Mutsaers [21] described the replacement by Cl radicals of OH groups on the TiO₂ surface:



If the catalyst's surface area is not large enough to trap all the Cl radicals produced, the radicals are released into the gas phase and trigger the formation of the undesirable products.

Adsorption of the Cl radical on the TiO₂ surface is likely to reduce the catalytic activity for long-term use. However, this did not happen in our case, i.e. the TiO₂ activity for TCE degradation has been maintained during a long experimental period (at least 2 weeks). Thus, the Cl radicals adsorbed or trapped on the TiO₂ surface can be removed as Cl₂ or HCl.

The O₂ in the gas phase also traps the released Cl radical. This reaction also inhibits the byproducts from being formed [22]:



Another possibility is the reaction of O₂ with the CHCl₂ or CCl₃ radicals, which is the precursor for the formation of CHCl₃ or CCl₄. This reaction would eventually produce CO₂. The excess of O₂ in the inlet gas, in fact, effectively reduces the concentration of CHCl₃ and CCl₄ in the outlet gas.

Although Nimlos et al. also used TiO₂ as the catalyst and obtained a large amount of phosgene with the stoichiometry ratios $\gamma_{\text{CO}_2:\text{TCE}}$ and $\gamma_{\text{COCl}_2:\text{TCE}}$ being 0.86 and 0.71 respectively [13], our catalyst produced none of it as the product. From calculations with the present results, the above ratios turned out to be almost 2.0 and 0.0 respectively. This means that the Cl-radical-initiated reaction is predominant in the system of Nimlos et al. They employed Degussa P-25 TiO₂ with a specific surface area of 56 m² g⁻¹. On the contrary, our synthesized TiO₂ catalyst fired at 300 °C has a specific surface area of 189 m² g⁻¹, this area being more than three times as large. Therefore, the Cl-radical-initiated reaction is what comes first and foremost in the system where the surface area is small. The high porosity and the large specific surface area are responsible for the high performance of our TiO₂ pellets in degrading VOCs.

The combination of the high oxygen mole fractions in the gas stream and/or the TiO₂ pellets fired at a lower temperature is very effective in suppressing the formation of such undesirable chlorinated byproducts as CHCl₃ and CCl₄. The formation of trace quantities of the minor byproducts does not prevent this promising technology from being put to practical use. The bed reactor packed with TiO₂ pellets prepared by sol-gel techniques together with UV light promises to be a simple and inexpensive method to degrade VOCs.

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