



DEGRADATION OF CARBON TETRACHLORIDE IN THE PRESENCE OF IRON AND SULPHUR CONTAINING COMPOUNDS

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ABSTRACT

The effect of several sulphur compounds: sodium sulphate, sodium sulphide, ferrous sulphide, pyrite and an organosulphonic acid on the kinetics of the iron (Fe^0) induced degradation of carbon tetrachloride was examined under aerobic conditions. It was observed that all of the sulphur compounds investigated significantly accelerated the reaction. The mechanisms of the processes studied as well as their possible influence on the efficiency of the iron-induced dehalogenation of pollutants, both *in situ* and in above-ground treatment are discussed.

INTRODUCTION

Pollution of groundwater and soil by halogenated organic compounds is a growing environmental concern. Since polyhalogenated pollutants often behave as Lewis acids (electron acceptors), they cannot always be destroyed by means of advanced oxidation processes (AOPs) [1]. Thus, there is great interest

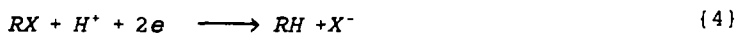
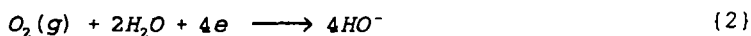
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in the reductive dehalogenation of these pollutants. Two such technologies have recently been proposed: (i) treatment of contaminated waste water and groundwater with photolytically generated hydrated electrons [2], and (ii) dehalogenation of pollutants by means of zero-valent iron [3-5]. The latter reaction, long known to organic chemists, has recently become the centre of attention [4-10] as a method of great potential, not only for the above-ground but also for *in situ* treatment of groundwater. However, problems associated with controlling the pH of the process and with the deactivation of the metal surface, make the practical application of this technique difficult.

Aqueous corrosion proceeds by the coupled electrochemical dissolution of iron (or another metal) and the reduction of substances present in its environment (for instance water or oxygen). Current flows in the metal from locations at which reduction occurs (cathodes) to locations at which oxidation predominates (anodes); a liquid layer serves to dissolve ions and act as a salt bridge. Typically, when iron is corroded, the anode reaction is:



so that solid iron goes into solution as Fe^{2+} ions. Several cathode reactions are possible:



The overall corrosion process is very complicated as it involves a number of different reactions [11] and leads to a significant increase in pH. In the absence of aggressive corrodents, the rate of rusting is usually quite small, due to the formation of a protective film of iron oxyhydroxides [12, 13].

It has recently been suggested [7] that sulphur, usually present as an impurity in metallic iron, plays an important role in the reduction process. Since various organic and inorganic sulphur compounds are present in the environment [14-18], some of which are known to contribute to the fate of halogenated pollutants [19-21], an understanding of their possible impact on the efficiency of the 'iron treatment' is very important. In this paper we report results of studies on the influence of sulphur compounds representing two principal classes of sulphur-bearing minerals, sulphate and sulphide ions, on the rate of the iron-induced degradation of carbon tetrachloride (CT) in water. We also discuss the mechanisms of these processes, and predict their influence on the efficiency of the iron-induced dehalogenation of pollutants, both *in situ* and in above-ground treatment.

MATERIALS AND METHODS

Chemicals

Zero valent iron powder (electrolytic, finer than 100 mesh), sodium sulphide, and ferrous sulphide were purchased from Fisher Scientific, pyrite (20 mesh) was obtained from American Minerals (Camden, N.J.), 4-(2-hydroxyethyl)-1-piperazine-ethanesulphonic acid (HEPES) and N- β -hydroxyethyl piperazine were purchased from Sigma Chemical Co. Ferric chloride was purchased from Baker, and the rest of the salts and organic solvents were from BDH, Canada. All chemicals were used as received. The solvent used was deionized water which had been further purified by a Barnstead's E-pure water purification system.

Apparatus

Samples were shaken in a Precision Scientific Shaking Water Bath 25 set at 25.0° C and 170 shakes per min. (horizontal movement). For samples containing metallic iron, the vials were centrifuged at 2500 rpm after shaking in an American Scientific Products Labofuge. The pH measurements were performed using a Corning pH Meter 320 equipped with a Corning pH combination electrode. The gas chromatograph (GC) used was a Hewlett Packard 5890 Series II equipped with an electron capture detector and an on-column injection port, and was attached to a HP 3396 Series II integrator. The carrier gas was an ECD grade helium and the head pressure was set at 25 kPa. Matheson grade nitrogen gas was used for the operation of the ECD detector. The fused silica column used for separation was a DB-5, 30.0 m x 0.53 mm, 5 μ m film column from Chromatographic Specialties. A 2.0 m x 0.53 mm deactivated precolumn was placed ahead of the analytical column, and the two were attached by a glass press fit connector, both of which were from Chromatographic Specialties.

General Procedure

Degradation reactions of aqueous carbon tetrachloride (CT) were performed in the presence of zero-valent iron (Fe^0), pyrite (FeS_2) or other sulphur-containing compounds. 5.0 g of Fe^0 , FeS_2 or FeS was placed in a 25 ml vial along with a known amount of a salt ($c = 0.05$ M) and the vial was filled with the CT (1.108 ppm) solution so that there was no headspace. The vial was then sealed with a rubber/teflon septum and the aluminum lid was crimped shut. Vials containing heterogeneous mixtures were manually rotated five times. Then, the samples were quickly placed in the shaker. After the allotted shaking time the samples were put in the centrifuge for 5 min. The total times then included both shaking and centrifuging. For compounds which were soluble in water, a 2.216 ppm solution of CT and a 0.1 M solution of salt were prepared and the vials were completely filled with equal amounts of each.

Analytical Methods

Determinations of the degradation of CT into its less chlorinated homologs were carried out by GC analysis of direct injections of the water samples. The separations were done isothermally with a column temperature of 102° C, an injection port temperature of 96° C, and detector temperature of 300° C. Immediately after centrifugation the samples were decrimped and 1.0 µl of this solution was injected into the GC. Samples containing insoluble salts and/or iron metal were filtered using syringe (nylon, 25mm, 0.2 µm) filters. Each concentration measurement represented the mean of two or more replicate GC runs. Replicate measurements usually agreed within ± 5%.

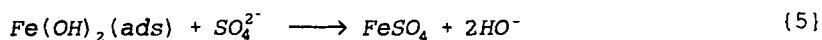
Calculations of Overall Observed rate Constants

For each sample analyzed for the concentration of CT, an observed pseudo-first-order rate constant was obtained from a plot of $\ln(C_0/C_t)$ vs t . For each sample, an overall observed rate constant k was estimated by taking the arithmetic mean of the k_i values of several samples for which $C_t \leq 0.95 C_0$ (the accuracy of C_0 was derived from the precision of the GC measurements (± 5%)). Note that the rate constants k thus obtained represents the sum of the actual rate constants for all reactions taking place in the system under investigation.

RESULTS AND DISCUSSION

As can be seen from Fig. 1 and Table I, the rate k of the first stage of reaction between CT and Fe^0 was relatively high, and exhibited a first-order dependence on substrate concentration. However, as the pH of the solution increased, the rate of degradation was greatly reduced. The addition of sodium sulphate to the system showed a slight effect on the initial rate constant k . At higher pH, however, the presence of the salt clearly accelerated the process, resulting in a significantly reduced time τ_{s0} (Table I) for iron-induced degradation of CT. As a control, sodium sulphate (at the same concentration) was added to the solution of CT in the absence of zero-valent iron, and showed no effect.

Sulphate (SO_4^{2-}) is associated with near-surface and sedimentary environments. It arises from atmospheric deposition of oceanic aerosols and the leaching of sulphate minerals like gypsum. It is also produced by the oxidation of metal sulphides which are present in small amounts in many rock types. Its natural concentration is usually lower than 300mg/L, but may reach up to 200,000mg/L in some places as a result of acid mine drainage [15-18]. Sulphate is known to remove iron oxides and hydroxides formed on the surface of iron [12, 24]:



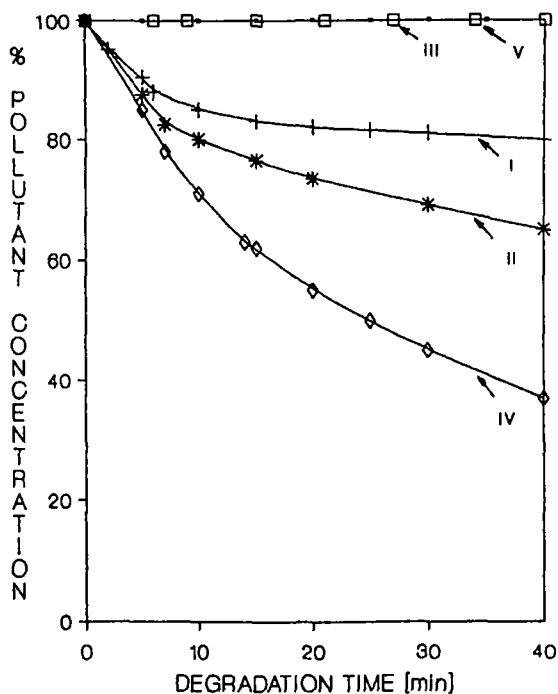
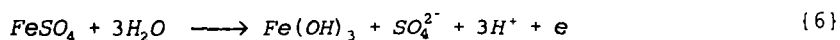


Figure 1. Degradation of CT (1.108ppm) in the presence of: (I) +--+ Fe⁰ (5 g/25ml); (II) -x- -x- Fe⁰ (5g/25ml) and Na₂SO₄ (c = 0.05M); (III) ----- Na₂SO₄ (c = 0.05M); (IV) <-<- Fe⁰ (5g/25ml) and HEPES (0.05M); (V) ▣-▣ HEPES (c = 0.05M).

Oxidative hydrolysis of FeSO₄ leads to the formation of ferric hydroxides and to the regeneration of the sulphate ions, which initiate the chain reaction.



Thus, the effect of sulphate on the rate of the CT degradation, shown in Fig.1 is probably due to destruction of the protective rust film, and the formation of a more soluble corrosion product. Recently, Schreier and Reinhard reported [10] that addition of an organic buffer 4-(2-hydroxyethyl)-1-piperazine-ethanesulphonic acid, HEPES, was apparently required for the iron-induced dehalogenation of tetrachloroethylene. Since some organosulphur compounds are known to accelerate the corrosion rate [12], we hypothesized that the observed effect might have been connected to the presence of the sulphonic acid group in the molecule of HEPES. As can be seen from Fig. 1 and Table I, the iron-induced degradation of CT in the solution of HEPES was much faster than was that in deionized water.

Table I. Degradation of CT (1.108ppm) in the presence of various reducing agents^{a)}. Overall observed rate constant k , half-life time, $\tau_{1/2}$ ($\tau_{1/2} = 0.693/k$), and time τ_{50} required for the degradation of 50% of CT.

Reductant	k (h^{-1})	$\tau_{1/2}$ (min)	τ_{50} (min)
Fe^0	1.77 0.07	23.5	> 240
$\text{Fe}^0 + \text{Na}_2\text{SO}_4$	1.82 0.05	22.9	~ 90
$\text{Fe}^0 + \text{HEPES}$	2.45 0.08	17	~ 25
$\text{Fe}^0 + \text{Na}_2\text{S}$	3.98 0.07	10.5	~ 12
Na_2S	1.89 0.05	22	~ 24
$\text{Fe}^0 + \text{FeS}^{\text{a)}}$	2.15 0.10	19.3	~ 95
$\text{FeS}^{\text{b)}}$	1.73 0.05	24	> 240
$\text{Fe}^0 + \text{FeS}_2^{\text{c)}}$	1.89 0.08	22	~ 70
$\text{Fe}^0 + \text{FeS}_2^{\text{d)}}$	3.20 0.05	13	~ 45
$\text{FeS}_2^{\text{e)}}$	1.73 0.08	24	> 210
$\text{FeS}_2 + \text{Fe}^{3+ \text{ f)}$	4.62 0.05	9	~ 90
$\text{FeS}_2 + \text{Fe}^{2+ \text{ g)}$	2.31 0.06	18	~ 150

^{a)} Amount of reductant(s) in each vial (25ml):

^{a)} 5g of Fe^0 and 0.199g of FeS (0.05 M), $\text{FeS}/\text{Fe}^0 = 0.038$; ^{b)} 5g of FeS ; ^{c)} 5g of Fe^0 and 0.15g (0.05M) of FeS_2 , $\text{FeS}_2/\text{Fe}^0 = 0.029$; ^{d)} 5g of Fe^0 and 0.6g (0.05M) of FeS_2 , $\text{FeS}_2/\text{Fe}^0 = 0.107$; ^{e)} 5g of FeS_2 ; ^{f,g)} 5g FeS_2 and 25ml of a Fe^{3+} or Fe^{2+} ($c = 2.5 \times 10^{-4}\text{M}$) solution, respectively.

The effect was obviously dependent upon an interaction between Fe^0 and the sulphonic acid group of HEPES, since no degradation of CT was observed in HEPES solution alone, or in solutions containing N- β -hydroxyethyl-piperazine (both in the presence and absence of zero-valent iron). We have also noticed that, during the iron induced degradation of CT, carried out in the presence of HEPES, some colloidal sulphur was formed, and the surface of the iron turned black, possibly indicating the presence of FeS . A similar change of colour of the iron surface during the degradation of PCE in a HEPES solution, has been observed by Schreier and Reinhard [10]. Thus, it seems that the effect of HEPES may result not only from its buffering properties (pH ~ 6.5) but also from the iron-induced reduction of the sulphonic acid group to produce the sulphide ion, a strong reducing agent. The iron induced transformation of HEPES will be studied in detail in the near future.

As can be seen from Fig. 2 and Table I, the iron-induced degradation of CT in oxygenated water, in the presence of sodium sulphide, was quite rapid (at pH ~ 12.4). This behaviour can be attributed to the reaction between sodium sulphide and CT and to sulphide induced corrosion of iron.

The sulphide reactivity is very much pH dependent, which can be predicted from a knowledge of E_{HOMO} for each species (H_2S , HS^- and S^{2-}) [23]. Since E_{HOMO} of S^{2-} (+6.1eV) is well above the E_{LUMO} of the common oxidants, S^{2-} can easily donate an electron (π) pair to a Lewis-acid-like oxygen or to a halogenated organic compound. The HOMO of HS^- (-2.5eV), which is predominant at neutral pH, is of similar energy to the LUMO of the oxidants, and therefore sulphide is expected to be quite reactive also at neutral pH. However, since the HOMO of H_2S (-10.47eV) is much lower in energy than the LUMO of the common natural oxidants, sulphide is less reactive at low pH.

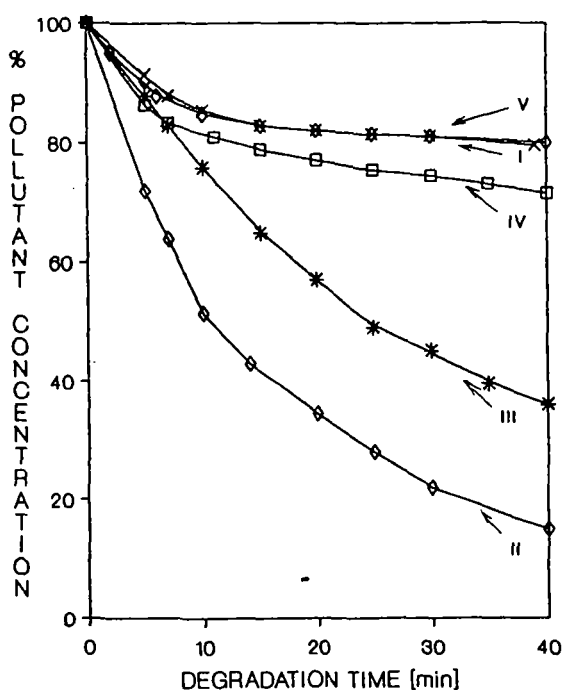
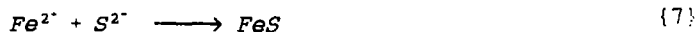


Figure 2. Degradation of CT (1.108ppm) in the presence of: (I) Fe^0 (5 g/25ml); (II) Fe^0 (5g/25ml) and Na_2S ($c = 0.05\text{M}$); (III) Na_2S ($c = 0.05\text{M}$); (IV) Fe^0 (5g/25ml) and FeS (5g); (V) FeS (0.15g/25ml, 0.05M).

In aerated solutions the oxygenation of the chemisorbed sulphide enhances both the depolarization of the hydrogen evolution reaction and anodic dissolution; the corrosion rate is thus accelerated [23]. The solid product of the reaction [7], ferrous sulphide (FeS), has reducing properties, and may further

contribute to the degradation of CT. Degradation of CT in the presence of FeS and a Fe⁰/FeS mixture is shown in Fig. 2. (As can be seen from Fig. 3, no significant increase in pH is observed when a Fe⁰/FeS mixture is used).



It should be noted here that in deoxygenated waters the sulphide ions may act as a catalyst poison, inhibiting the recombination of cathodic hydrogen atoms with H₂ molecules [12].

The Earth's mantle and core are rich in metal sulphides with pyrite (FeS₂) being the most abundant and mined in many countries [17]. In nature, pyrite is one of the prominent geochemical electron donors and so it is expected to play an important role in the natural decay of many pollutants, including carbon tetrachloride [21d]. We have found that an addition of pyrite to zero-valent iron, significantly reduces the time associated with the aerobic degradation of CT (Fig. 4, Table I).

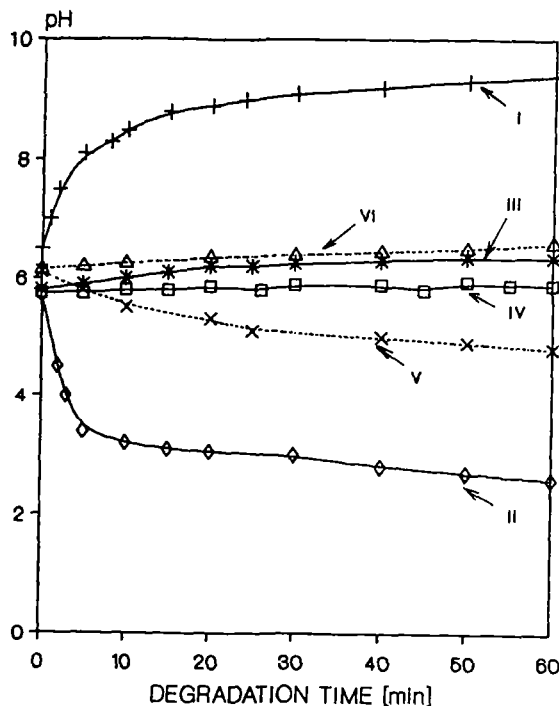
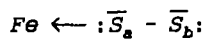


Figure 3. pH changes observed during degradation of CT ($c = 1.08\text{ppm}$) in the presence of: (I) $-\text{+}-$ Fe⁰ (5 g/25ml); (II) $\diamond-\diamond$ FeS₂ (5 g/25ml); (III) $*-*$ Fe⁰ (5g/25ml) and FeS₂ (0.029g/25ml, $c = 0.05\text{M}$); (IV) $- \cdot - \cdot -$ Fe⁰ (5g/25ml) and FeS₂ (0.6g/25ml, $c = 0.2\text{M}$); (V) $\times-\times$ FeS (5g/25ml); (VI) $\triangle-\triangle$ Fe⁰ (5g/25ml) + FeS 0.199g (0.0%M).

There are several possible reasons for the observed effect. Pyrite can be considered a polysulphide ion, S_2^{2-} , bound to an Fe^{2+} ion [24]. It has a broad ESCA valence band, attributable to the HOMO of S_2^{2-} near $-3.9eV$. In the Lewis acid-base sense, the unit of pyrite can be represented as:



with a lone pair of electrons from S_a donated to Fe^{2+} . Consequently, there is a slight negative charge on the pyrite surface due to S_b . In the structure presented above, S_b has a lone pair of electrons (from a π^* HOMO) available for donation to a vacant orbital of a Lewis acid (metal ions like Fe^{2+} or Fe^{3+} , singlet oxygen, or halogens) [22]. Under aerobic conditions, pyrite undergoes oxidation to sulphate and ferric ion:

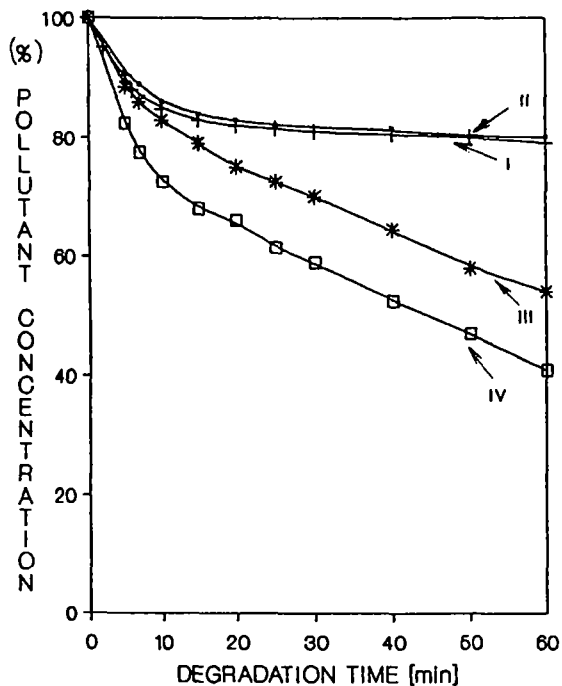
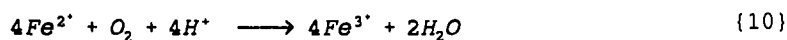
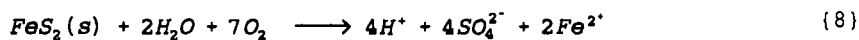
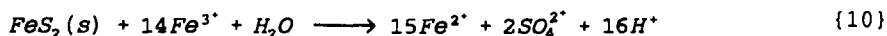


Figure 4. Disappearance of CT (1.108ppm) in the presence of: (I) $+ + Fe^0$ (5 g/25ml); (II) $- - - - - FeS_2$ (5 g/25ml); (III) $- * - * - Fe^0$ (5g/25ml) and FeS_2 (0.029g/25ml, $c = 0.05M$); (IV) $- \square - \square - Fe^0$ (5g/25ml) and FeS_2 (0.6g/25ml, $c = 0.2M$).

The pH of the solution decreases (Fig. 3), i.e. the pH effect of steps {8,9} is opposite to that observed during the oxidation of zero-valent iron {2,3}.

The ferric ion, Fe^{3+} , formed both in reaction (9) and during the corrosion of iron zero further dissolves pyrite (10), leading to a further decrease in pH and the production of sulphate and a reducing agent (Fe^{2+}):



Therefore, one can expect that as a result of reaction (10), the rate of the pyrite-induced degradation of organohalogen compounds should increase in the presence of ferric ion. Indeed, we have observed such an effect during our experiment with CT (Table I).

It has been reported by other researchers [8a] that chloroform ($CHCl_3$) is the main product of the iron-induced degradation of CT. It is also known that in oxygen deficient conditions, sulphide reacts (as electron donor or nucleophile) with volatile bromo- and chloroalkanes [16 - 18] often creating persistent and hazardous sulphur-containing compounds. Sulphide-induced transformation of CT is known to produce a toxic [25] intermediate, carbon disulphide [CS_2]. Identification of products and determination of the accurate mass balance was not included in the studies described in this paper. However, analysis of our GC data suggests, that, while almost no chloroform was formed during the reaction between CT and Na_2S , FeS or FeS_2 (under oxic conditions), this compound was the main product of the reaction when mixtures of Fe^0/FeS_2 or Fe^0/FeS were used. More detailed studies on this subject will be carried out in the near future.

CONCLUSIONS

In summary, addition of any of the sulphur compounds investigated, namely: sulphate, organosulphonic acid (HEPES), sulphides (Na_2S and FeS) and pyrite accelerated the iron induced degradation of carbon tetrachloride under aerobic conditions. Thus, it can be expected that the efficiency of such a treatment *in situ* will be significantly enhanced due to the presence of bacterial and fungal metabolisms that produce a large number of sulphur-bearing organic compounds. It is also anticipated that the degradation may be efficient in places rich with sulphur-containing minerals.

In both above-ground and *in situ* treatments, some addition of pyrite to the zero-valent iron should accelerate the treatment. Processes involving pyrite would regenerate ferrous ions (11), produce sulphate (8, 10) (which would remove the deactivating oxide film from the metal surface (5)) and control the pH of water.

It should be taken into account that during the water treatment some toxic sulphur derivatives may be formed. Thus, a careful identification of intermediates and products would be required.

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