A Mechanism for the Destruction of CFC-12 in a Nonthermal, Atmospheric Pressure Plasma

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The destruction of CFC-12 (CF_2Cl_2) has been studied in an AC, nonthermal, atmospheric pressure plasma reactor packed with barium titanate beads. The extent of the destruction in air ranges between 8% and 40% depending on the conditions. The decomposition products in air as determined by infrared spectroscopy are CO, CO_2, and COF_2. It is deduced that the undetected chlorine and fluorine is present as F_2 and Cl_2. A chemical mechanism for the decomposition is proposed. Large concentrations of NO, NO_2, and N_2O are also formed. Destruction in a stream of pure N_2 is about twice as effective as in air under corresponding conditions. The addition of a small amount of water (∼0.03%) or oxygen (∼0.02%) to the nitrogen carrier gas increases the destruction efficiency but the presence of molecular hydrogen (≤2%) brings about no enhancement. It is suggested that in all cases, the primary decomposition step involves dissociative electron attachment to the CF_2Cl_2. This is confirmed by the observed differences in the destruction in pure nitrogen and in air.

Introduction

There is an urgent need to develop efficient methodologies for the destruction of CFCs to prevent the release of such ozone-depleting substances into the atmosphere and their subsequent migration into the stratosphere. Various techniques including high-temperature incineration of gases and thermal plasma torches are used to deal with the various components. Particularly high temperatures (≥1250 °C) are needed to ensure that the halogenated components are safely destroyed without the formation of dioxins. It is against this background that many groups have investigated the prospect of using thermal and nonthermal plasma methods as an energy-efficient method of destroying CFCs.

In this paper, we report studies of the destruction by nonthermal, atmospheric pressure plasma of CFC-12, dichlorodifluoromethane (CF_2Cl_2), in various gas streams (air and nitrogen with the addition of oxygen, molecular hydrogen, and water) using an AC, packed-bed plasma reactor loaded with $BaTiO_3$ beads. Previous studies of the destruction of CF_2Cl_2 by plasma at atmospheric pressure include the use of microwave plasma,[1] thermal plasma torch,[2,3] dielectric barrier discharge,[4] and a pulsed corona discharge.[5] A packed bed, plasma reactor similar to that used in this experiment has been employed to study the destruction of CFC-113 ($CCl_2F{-}CClF_2$) at atmospheric pressure.[6] Gal' et al.[7] have studied the destruction of a range of CFCs including CFC-12 in an atmospheric pressure, nitrogen stream using a $BaTiO_3$ packed bed, plasma reactor. We present the first results for the destruction of CFC-12 in an air stream using a nonthermal, atmospheric pressure, plasma reactor packed with barium titanate beads. The effect of the addition of hydrogen and water to a nitrogen carrier gas has also been investigated. From these studies, we propose chemical mechanisms to explain the destruction pathways and the formation of the products that are observed. In particular, we focus upon the nature of initial decomposition of the CFC where there is some disagreement about the role played by different processes in the plasma decomposition of halogenated methanes.[7−9]

Experimental Section

The experimental arrangement is essentially that used previously.[8] The plasma source is a dielectric pellet-bed reactor consisting of a glass tube of 24 mm internal diameter with two electrodes ∼25 mm apart through which the gas passes. The space between the electrodes is packed with 3.5 mm diameter barium titanate beads. The diameter of the beads is chosen to allow for as large a number of beads as possible, thereby maximizing the number of contact points for the formation of discharges while not restricting the porosity of the reactor significantly. This balances the requirements of gas flow and having as uniform a discharge as possible. An AC voltage ($V_{\mathrm{pk-pk}} \approx 15$ kV) at a frequency between 10.25 and 13.25 kHz is applied between the electrodes. Using a digital storage oscilloscope (Tektronix TDS 3012), we record the current and voltage waveforms for the discharge by using a calibrated high-voltage probe and measuring the current across a 1 kΩ resistor in the return earth path from the reactor. The average power of the discharge is then obtained by integrating the product of voltage and current as a function of time.

A flow (0.25−1.5 L min^{-1}) of pure air or nitrogen at room temperature controlled by mass flow controllers (MKS Mass Flo) is blended with a small flow of gaseous CCl_2F_2 giving a concentration of ∼30−500 ppm entering the plasma reactor. Small amounts of hydrogen could be added directly to the nitrogen gas stream and also water by bubbling nitrogen through liquid water to investigate the effect of these additives on the processing. Nitrogen containing small amounts of oxygen was made by mixing appropriate amounts of pure nitrogen and air. The gas mixture was maintained at a pressure of ∼1 bar. For a total gas flow of 1 L min^{-1}, the residence time in the reactor is 0.25 s. CFC-12 (Argo International, >99% purity) was used as supplied. No attempt was made to further purify or dry the gas. The end products of the plasma processing were monitored on-

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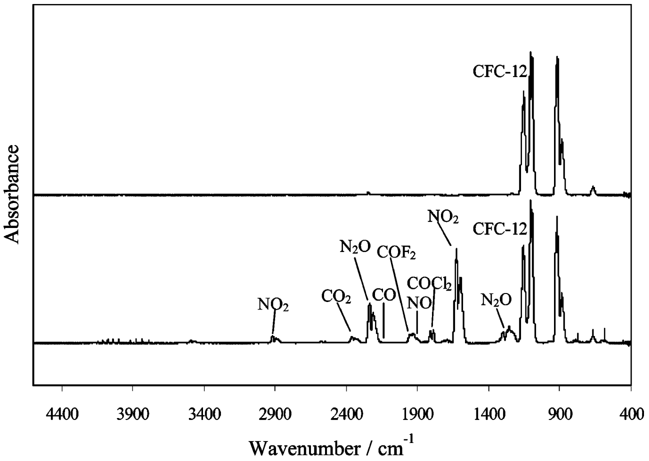

Figure 1. FTIR spectra of the end products of the plasma processing of CFC-12, dichlorodifluoromethane: (upper panel) plasma off and (lower panel) in undried air. Flow rate is 1 L min^{-1}. Resolution is 1 cm^{-1}.

TABLE 1: The Plasma Processing of CFC-12 in an Air Stream for Different Flow Rates and Different Initial Concentrations[a]

flow rate/ L min^{-1}	CFC-12 input	% destruction	CO	CO_2	COF_2	NO	NO_2	N_2O
1.5	506	8	12	3	21	129	265	128
1	460	11	12	8	28	159	311	169
0.5	445	23	23	86	42	275	372	266
0.25	210	40	27	88	30	306	438	380

[a] Listed are the percentage destructions of the CFC and the yield of the products as detected by FTIR. All concentrations are in ppm.

line by infrared spectroscopy, using a long-path gas cell (2.76 m, Venus Series) and a Fourier Transform Infrared (FTIR) spectrometer (Shimadzu 8300) with a resolution of 1 cm^{-1}. Stainless steel, nylon, and PTFE tubing, valves, and fittings of 1/4 in. external diameter were used to handle the gases as appropriate. No attempt was made to bake or otherwise condition the surfaces of the system.

Results

Figure 1 shows a comparison of the FTIR spectrum obtained for CFC-12 in an air stream with and without plasma processing. Table 1 details the destructions and detected yields of products for the processing of CFC-12 in air. The percentage destruction ranges between 8% and 40% depending on the initial concentration and the flow rate, with the highest percentage destruction being obtained for the lowest flow rate of 0.25 L min^{-1} and an initial CF_2Cl_2 concentration of 210 ppm. The detected products for the processing in air at flow rates of 1.0−1.5 L min^{-1} were CO (∼30%), CO_2 (∼12%), and COF_2 (∼58%) accounting for >90% of the destroyed carbon; COF_2 was the only detected halogen-containing end product and accounts for ∼55% of the removed fluorine. A peak at ∼1800 cm^{-1} is observed in some spectra (Figure 1) that can be ascribed to the production of phosgene, $COCl_2$. However, this product is an impurity that results from the small residual presence of water (<200 ppm) in the air stream. If the air is further dried to water levels <10 ppm, this feature disappears and is not therefore a product of the plasma destruction of CFC-12 in dry air. There was also substantial production (∼500−1000 ppm) of nitrogen oxides, principally NO_2 (∼50%) with NO (∼25%) and N_2O (∼25%). For the lower flow rates where the residence time in the plasma reactor is longer, more of the destroyed carbon becomes CO_2 rather than COF_2 and CO and there is higher production of the oxides of nitrogen (∼1500 ppm).

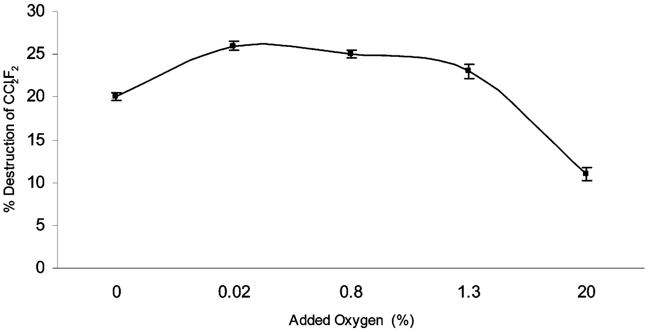

Figure 2. The variation of the percentage destruction of CFC-12 for plasma processing of an initial concentration of ∼420 ppm in an atmospheric pressure mixture of nitrogen and added oxygen at a total flow rate of 1 L min^{-1}. Listed are the percentage destructions of the CFC. The errors represent one standard deviation. Note that the abscissa scale is nonlinear.

TABLE 2: The Plasma Processing of ∼360 ppm CFC-12 in a Mixture of Nitrogen with Added Water at a Total Flow Rate of 1 L min^{-1} [a]

% water	CFC input	% destruction	CO	CO_2	COF_2	HCN	HCl	HF	N_2O
0	332	15 ± 0.5	23	3	18	4	0	0	30
0.03	382	29 ± 0.5	32	7	18	5	45	24	56
0.05	367	26 ± 0.5	28	7	20	5	57	39	64
0.09	359	25 ± 0.5	34	11	23	7	35	16	80

[a] Listed are the percentage destructions of the CFC and the yield of the products as detected by FTIR. All concentrations are in ppm. The errors represent one standard deviation.

In a second series of experiments, we investigated the effect of oxygen on the plasma destruction of CFC-12 by using a mixture of oxygen and nitrogen as the carrier gas in which the percentage of oxygen ranged from 0% to 1.3%. These results are shown in Figure 2 together with the data for air. It can be seen that the destruction is greatest for a small addition of oxygen (< 0.08%) and then decreases to the lower value measured for air, which is about half that in a stream of pure nitrogen.

Small amounts of hydrogen (≤2%) were also added to the nitrogen carrier gas but no change was observed in the magnitude of the destruction or the identity of the end products. Similarly, small amounts of water (<0.03%) were added to the nitrogen bringing about a significant increase in destruction efficiency from 15% to 29% (see Table 2). The presence of HF and HCl was detected when water was added to the carrier gas. Of the destroyed fluorine content of the CFC-12, about 34% is accounted for by COF_2 and HF. HCl accounts for ∼20% of the destroyed chlorine. (Our detection sensitivities for HF and HCl are ∼20 and 15 ppm, respectively.) N_2O is formed but no other oxides of nitrogen. A summary of the dependence of the destruction efficiency with the identity of the carrier gas for the nonthermal, atmospheric pressure plasma processing of CFC-12 is shown in Figure 3.

For the experiments reported here, the power supplied to the plasma was measured as 1.08 W irrespective of the flow rate or identity of the carrier gas. In terms of reduced energy density, this ranges between 40 and 260 J L^{-1} corresponding to a minimum energy requirement of between 284 and 338 eV per molecule of CF_2Cl_2 removed in air and nitrogen, respectively.

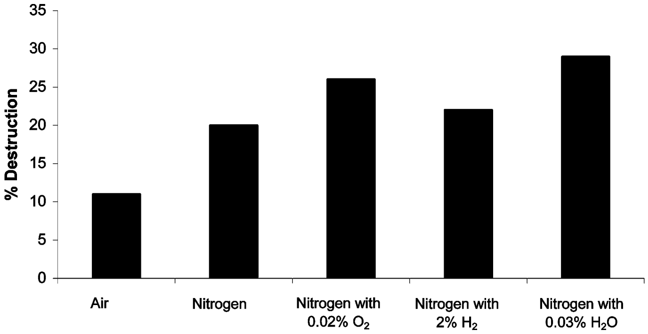

Figure 3. A comparison of the percentage destruction of CFC-12 in a nonthermal, atmospheric pressure plasma for different compositions of the carrier gas at a flow rate of 1 L $\min^{-1}$.

Discussion

Complete oxidation of CFC-12 in air can be globally represented by the process

$$CCl_2F_2 + O_2 \rightarrow CO_2 + Cl_2 + F_2 \qquad (1)$$

Our detection of COF_2 and CO as carbon-containing species indicates that the oxidation is incomplete under our conditions. In a nonthermal plasma, highly energetic electrons are produced which dissociate and excite the major components in the gas stream creating ground and electronically excited oxygen and nitrogen atoms and molecules (O(^{3}P and ^{1}D), $O_2(a^1\Delta)$, N(^{4}S, ^{2}D, ^{2}P), and $N_2(A^3\Sigma_u^+)$) and simple free radicals (e.g., OH) when water is present. Excited states are generally quenched rapidly at atmospheric pressure and do not contribute significantly to reaction with the possible exception of the triplet metastable state of nitrogen, $N_2(A^3\Sigma_u^+)$, and excited nitrogen atoms, N(^{2}D).

The primary decomposition step for CF_2Cl_2 in air is then either by low-energy, electron impact dissociation involving dissociative electron attachment[10] followed by neutralization of the resulting negative ion or by collision-induced dissociation with metastable triplet molecular nitrogen, $N_2(A^3\Sigma_u^+)$, which has an excitation energy of 6.23 eV. The most likely end products for the dissociative channels are CF_2Cl and Cl in both cases because the C−Cl bond in CF_2Cl is much weaker than the C−F bond. Wang et al.[10] have shown that the dissociative electron attachment channel

$$e + CF_2Cl_2 \rightarrow CF_2Cl + Cl^- \qquad (2)$$

is exoergic. Although the overall rate coefficient for the quenching of $N_2(A^3\Sigma_u^+)$ by CFC-12 is large (1.5×10^{-13} cm^3 s^{-1})[11] and will involve the production of an excited state of CF_2Cl_2 by E → E transfer, it is uncertain what the fate of that excited state may be. The channel

$$N_2(A^3\Sigma_u^+) + CF_2Cl_2 \rightarrow CF_2Cl + Cl + N_2(X^1\Sigma_g^+) \qquad (3)$$

may be considered on energetic grounds. However, in their study of the plasma destruction of CF_2Cl_2 in nitrogen, Gal' et al.[7] have concluded that the extent of CFC-12 destruction by energy transfer from metastable nitrogen is negligible and that the dominant destruction process is dissociative electron attachment (reaction 2) followed by neutralization of the chlorine. This contrasts with the mechanism proposed for the plasma destruction of dichloromethane, CH_2Cl_2, studied by ourselves[8] and the group of Penetrante et al.,[9] where destruction in nitrogen carrier gas comes from reaction with nitrogen atoms and collisional destruction by metastable $N_2(A)$ rather than by electron attachment arising in part from the lower cross section for electron attachment for CH_2Cl_2[12] compared with CF_2Cl_2[10] ($\sim 1 \times 10^{-10}$ cm^3 s^{-1} compared to $\sim 1.6 \times 10^{-9}$ cm^3 s^{-1}). Additional support for the dissociation of CFC-12 being via electron impact comes from considering the behavior observed in gas streams containing oxygen where the reaction of $N_2(A^3\Sigma_u^+)$ with O_2 competes with reaction 3. This reaction has a larger rate coefficient (2.5×10^{-12} cm^3 s^{-1})[11] and one can estimate that if reaction 3 is responsible for the initial dissociation of CF_2Cl_2 that there should be a significant reduction (>1000) in the destruction of CFC-12 on going from a nitrogen gas stream to one that contains 20% O_2. In fact we observe that the destruction is only reduced by a factor of 2, indicating that the intial destruction step in the case of CF_2Cl_2 is by electron dissociation, reaction 2.

We can discount any destruction of CF_2Cl_2 by reaction with atomic oxygen as this process is too slow to compete with reaction 2. This parallels the conclusion made by Penetrante et al.[13] in their study of the destruction of CCl_4 in air using a pulsed corona discharge that dissociative electron attachment to CCl_4 will dominate atomic oxygen reactions in bringing about the initial decomposition of CCl_4. In the presence of oxygen, we observe significant formation of NO, NO_2, and N_2O. This arises because the excited-state nitrogen atoms can react with molecular oxygen to form NO, which is further oxidized to NO_2

$$N^*(^2D) + O_2 \rightarrow NO + O \qquad (4)$$

Further reaction of atomic nitrogen with NO_2 gives rise to N_2O

$$N^*(^2D) + NO_2 \rightarrow N_2O + O \qquad (5)$$

which can also be formed as a minor channel of the reaction of metastable triplet *A* state if nitrogen reacts with molecular oxygen ($k = 5 \times 10^{-14}$ cm^3 s^{-1})[14]

$$N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2O + O \qquad (6)$$

Wang et al.[15] in their recent study of the destruction of a $CF_2Cl_2/O_2/Ar$ in a low-pressure, RF plasma discharge have presented a chemical mechanism for the decomposition of CF_2Cl_2 in an oxygen environment. Following the initial decomposition of the CFC by reaction 2, they suggest that the resulting CF_2Cl radical can be decomposed by atomic or molecular oxygen to give COF_2

$$O, O_2 + CF_2Cl \rightarrow COF_2 + Cl, ClO \qquad (7)$$

Under the higher pressure conditions of our atmospheric pressure plasma, three-body reaction with O_2 will dominate to form the adduct, CF_2ClO_2,

$$O_2 + CF_2Cl \rightarrow CF_2ClO_2 \qquad (8)$$

This adduct can then react with NO or ozone to yield COF_2

$$CF_2ClO_2 + NO \rightarrow NO_2 + CF_2ClO \rightarrow NO_2 + Cl + COF_2 \qquad (9)$$

$$CF_2ClO_2 + O_3 \rightarrow ClO_2 + O_2 + COF_2 \qquad (10)$$

The COF_2 radical can be further oxidized along with any smaller radicals such as CF and CF_2 to produce CO and CO_2. This gives the range of carbon-containing end products that we observe in the presence of oxygen. The absence of any phosgene, $COCl_2$, or any halocarbon products confirms the original dissociation channel and the subsequent chemistry. The fluorine that is not present as COF_2 is most likely to be in the form of F_2 (undetectable by FTIR). The total absence of any detectable, chlorine-containing end products in our experiments suggests that Cl_2 (undetectable by FTIR) is the likely end product formed by recombination of chlorine atoms or by reactions involving the intermediates ClO and ClO_2.

We can compare our detected end products with those obtained in other atmospheric pressure plasma studies. In the thermal microwave plasma destruction of 2−8% CF_2Cl_2 in air, Jasinski et al.[1] found that COF_2, $COCl_2$, Cl_2, CO, and CO_2 were produced together with NO, NO_2, and N_2O_4. They achieved up to 100% destruction with microwave powers of 100 W. We agree with these findings except for the production of phosgene, $COCl_2$, and the absence of N_2O, which may result from the different excited species created in a microwave plasma compared with our dielectric packed bed plasma. Jian et al.[4] studied the destruction of 2.6% CF_2Cl_2 in air in an atmospheric pressure, dielectric barrier discharge. For residence times of greater than 30 s, they could achieve complete destruction of the CFC yielding COF_2, COFCl, and CF_4.

We now comment on the effect of the addition of oxygen and water to the nitrogen carrier gas. The addition of small amounts (0.02−0.03%) of both oxygen and water brings about an enhancement of the CFC-12 destruction that is slightly greater for the addition of water than for the addition of oxygen (Figure 3). The increase in CFC destruction with the small addition of oxygen which is then reduced for further addition of oxygen so that destruction in air is about 50% less efficient than for pure nitrogen is reminiscent of the behavior observed in our study of the destruction of dichloromethane.[8] The mechanism of the destruction of CFC-12 in oxygen has been discussed above. The reduction in destruction efficiency in air when there is a large amount of oxygen present comes from the competition for electrons in the plasma discharge between CF_2Cl_2 and the oxygen. Reduction in the electron attachment to CF_2Cl_2 will affect the overall amount of dissociation by this channel. The increase in atomic oxygen produced in the air discharge will have no effect on the degree of CFC-12 dissociation as attack by O atoms on the CFC plays no part in its destruction.

For the destruction of CFC-12 with water added to the nitrogen carrier gas stream, we observe the additional production of HCl and HF as end products. The overall oxidation of CF_2Cl_2 by water can be represented as

$$CF_2Cl_2 + H_2O \rightarrow CO_2 + HF + HCl \tag{11}$$

In our plasma processing, this process is incomplete as we also detect CO and COF_2 which have not been completely converted to CO_2 and the amount of HF and HCl formed does not account for all the fluorine and chlorine of the destroyed CFC-12, which is probably because of the production of F_2 and Cl_2 that are not detectable by infrared spectroscopy. The dissociation of water in the discharge will produce hydrogen atoms and hydroxyl radicals that are responsible for the formation of HF and HCl by processes such as the following:

$$COF_2 + H \rightarrow COF + HF \tag{12}$$

$$COF + OH \rightarrow CO_2 + HF \tag{13}$$

$$OH + ClO \rightarrow HCl + O_2 \tag{14}$$

$$H + X_2 \rightarrow HX + X\ (X \equiv Cl, F) \tag{15}$$

The small amounts of HCN that are formed are reminiscent of the nonthermal, atmospheric plasma destruction of dichloromethane[8] and methane[16] in pure nitrogen where HCN formed by reactions of electronically excited nitrogen atoms and molecules was the major carbon-containing product and disappeared when oxygen ($\geq$1%) was added. In the present studies, the addition of $<$0.1% of water means that we may still be in a transitional stage and might expect the formation of HCN to cease with increased concentration of oxidant. The small amounts of N_2O, CO, CO_2, and COF_2 that are observed during the plasma processing in a nitrogen stream are thought to result from the reaction of excited-state nitrogen and lattice oxygen species in the $BaTiO_3$ beads liberating reactive oxygen as was observed by Ogata et al.[17] and ourselves[16] in studies of methane dissociation in a barium titanate packed bed plasma reactor.

Finally, we observed that the addition of up to 2% of molecular hydrogen to the nitrogen carrier gas has no significant effect on the destruction efficiency of the CFC-12. Low-pressure RF studies of the decomposition of CFC-12/hydrogen mixtures in argon[15,18] where the hydrogen concentration is several times that of the CFC show that destruction of up to 96% can be achieved with 85 W of input power yielding CH_4, C_2H_2, HCl, HF, and carbon soot. The addition of hydrogen increases the destruction from about 90% and is optimal for a CF_2Cl_2/H_2 ratio between 0.5 and 2.0. The reaction of the CF_2Cl radical from reaction 2 with hydrogen atoms and molecules is responsible for the formation of the hydrocarbon and hydrogen halide products. In our system where the CF_2Cl_2/H_2 ratio is less than 0.02, it is likely that a sufficient concentration of H from electron dissociation of H_2 to enhance the normal decomposition operative in nitrogen is never achieved.

In terms of energy costs, the corona studies[5] found a value of 2000 eV/molecule for the destruction of CF_2Cl_2 in humidified air, compared with our value of 284−338 eV/molecule. In contrast, destruction by the thermal plasma of a microwave torch[1] is at an energy cost for the CF_2Cl_2 destruction of 4 kW h kg^{-1} or 0.05 eV/molecule.

Conclusions

The effectiveness of nonthermal, atmospheric pressure plasma processing for the destruction of CFC-12, CF_2Cl_2, has been demonstrated in gas streams of air and nitrogen. The initial destruction step for the CFC comes about by dissociative electron attachment rather than collision-induced dissociation by the metastable $N_2(A)$ state or by reaction with atomic oxygen. The subsequent chemistry depends on oxygen-containing species which come from dissociation of either air or water in the plasma. Under these conditions, complete destruction would yield CO_2, Cl_2, and F_2 (or HCl and HF in the case of water). However, short residence times or insufficient energy means that oxidation is incomplete and the products also include COF_2 and CO. An undesirable byproduct of the plasma processing is the coproduction of high levels of nitrogen oxides especially in the case of processing in air. We are currently investigating the hybrid technique of plasma-assisted catalysis in which the NOx will be converted into N_2 on a suitable catalyst, which may also enhance the destruction of the CFC thus increasing the overall energy efficiency of the process.

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