Properties of Fluoroformyl Hypofluorite, FC(O)OF, Revisited

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Received May 27, 1994[®]

It is shown that the new compound FC(O)OOF is formed during the synthesis of FC(O)OF and decomposes rapidly into FC(O)F and O_2. Its instability is responsible for that previously attributed to FC(O)OF reported in the literature. After an improved purification, the properties of FC(O)OF were reinvestigated and for the first time two conformers, *cis* and *trans*, were detected by ^{19}F NMR spectroscopy. From the gas phase ^{19}F NMR spectra at different temperatures, the barriers of internal rotation were determined to be 35.0 and 40.4 kJ mol^{-1} for *cis*- and *trans*-FC(O)OF, respectively. The mechanisms of formation of FC(O)OF and its precursor FC(O)OOC(O)F were investigated using isotopically enriched $C^{18}O$ and $^{18}O_2$ in the synthesis.

Introduction

Until very recently fluoroformyl hypofluorite,[1] FC(O)OF, was considered to be an unstable molecule.[2] However, we were able to show that FC(O)OF of high purity can be manipulated in a well-conditioned vacuum glass line without any appreciable decomposition at room temperature for more than 8 h.

The underlying chemistry and physics of this molecule deserve a detailed analysis because FC(O)OF is an important precursor in the synthesis of difluorodioxirane (DFDO),[2] an isomer that was recently postulated as an intermediate in the possible formation of ozone by CF_2 in the stratosphere.[3] Also it is important as a precursor to FC(O)O• radicals, whose catalytic activity toward ozone and general behavior toward atmospheric trace gases are a subject of high current interest.[4–6]

The kinetic stability of FC(O)OF allowed us to detect two conformers by IR, Raman, and NMR spectroscopy and to further study and characterize some of its physical properties as well as the equilibrium involved in the *cis*–*trans* isomer interconversion (eq 1). Results from this extensive characterization are reported in this paper.

(1)

Experimental Section

Caution! Since many of the compounds involved in the synthesis and purification are potentially explosive, they must be handled with appropriate shielding, eye protection, and gloves.

Any apparatus used (whether stainless steel, quartz, or Duran glass) must be thoroughly cleaned and passivated with FC(O)OOC(O)F prior to its use to avoid unwanted decomposition.

Materials/Chemicals. FC(O)OF was synthezised by the photochemical fluorination of bis(fluoroformyl) peroxide.[1] A 1000 mL quartz glass round flask was used, and the typical mixtures (200 mbar of peroxide and 200 mbar of F_2) were irradiated for 3 h with a 75 W low-pressure Hg lamp (Gränzel, Karlsruhe). Fluorine (Solvay) was measured by PVT and manipulated in a stainless steel vacuum line equipped with a diaphragm pressure gauge (Medas SP65). After the excess F_2 was pumped out at 77 K, the products were separated by fractional condensation in vacuo. The different fractions retained in traps at 153, 123, and 77 K were identified by IR spectroscopy using a 20 cm cell with AgCl windows. Repeated fractionation of the 123 K fraction resulted in FC(O)OF containing FC(O)F and CO_2 as the only detectable impurities. Separation from these impurities was achieved by taking advantage of the high evaporation speed of FC(O)OF associated with its low melting point (see Results and Discussion) and the comparatively low sublimation speeds of FC(O)F and CO_2. For this purpose, the mixture was condensed onto the upper part of the wall of a finger trap. After removal of the liquid nitrogen Dewar vessel, FC(O)OF was allowed to flow down to the lower part of the finger trap, which was rapidly warmed up to 273 K with a heat gun. In this manner, FC(O)OF is evaporated much more rapidly than FC(O)F and CO_2, which are left as solids in the cold top part of the trap.

^{18}O-substituted FC(O)OF was prepared from two different ^{18}O sources. $C^{18}O$ (>98%, Ventron) was used in an attempt to produce FC(^{18}O)OF, and $^{18}O_2$ (>99%, Ventron), in an attempt to produce FC(O)^{18}OF. Into a 500 mL quartz glass round flask, containing a mixture of CO and O_2 (53 and 80 mbar) was very slowly introduced F_2 (55 mbar) to form bis(fluoroformyl) peroxide within 1 h at room temperature. An additional 40 mbar of F_2 was added, and the mixture was photolyzed for 2 h. The purification of FC(O)OF was carried out as described above.

Instrumentation. (a) NMR Spectroscopy. The ^{19}F NMR spectra of pure liquid samples at 183 K were recorded by using a Bruker MSL 200 spectrometer and a Bruker $^{19}F/^{1}H$ dual probe head operating at 188.31 MHz. A 5 mm diameter tube which contained the hypofluorite sample was centered inside a 10 mm tube containing the lock CD_2Cl_2 and the reference $CFCl_3$. Low-temperature studies were carried out by using a Bruker variable-temperature controller with a copper–constantan thermocouple. The high vapor pressure of FC(O)OF did not allow measurements on the liquid above 223 K.

For each spectrum, 64 scans were accumulated in a 64 kbyte memory with a waiting time of 5 s between two scans. The time resolution was set to 10 μs, yielding a spectral resolution of 0.61 Hz/point. Because of this rather high spectral resolution, the spectra were accumulated in two parts, from 291 to 188 ppm and from 18 to −88 ppm. Overview spectra were recorded with a spectral resolution of 3.052 Hz/point. The pulse length was set to 3.5 μs.

In the gas phase, the spectral line width, caused by fast spin–lattice relaxation (T_1 < 20 ms), was larger than 200 Hz. Therefore, a spectral

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® Abstract published in *Advance ACS Abstracts,* December 15, 1994.

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0020-1669/95/1334-0603$09.00/0

Table 1. ^{19}F NMR Data for FO, FOO, and FC(O) Compounds

X	δ(XOF),[a] ppm	δ(XOOF),[a] ppm	X	δ(XC(O)F),[a] ppm	$J(^{13}C, F)$, Hz
F_3C	150[b]	292[c]	F	−23.0[d]	309[d]
F_5S	189[b]	330[c]	FC(O)OO	−37.9[e]	302[e]
FO_2S	249[b]	291[b]	*cis*-FO	−21.2[e]	330[e]
O_2N	219[f]		*trans*-FO	−38.3[e]	300[e]
cis-FC(O)	223.0[e]		FOO	−31.3[e]	312[e]
trans-FC(O)	201.3[e]	271.7[e]			

[a] Chemical shifts relative to $CFCl_3$. [b] Reference 7. [c] Reference 8. [d] Reference 9. [e] This work. [f] Reference 10.

resolution of 3.052 Hz/point and a pulse repetition time of 1 s were used as acquisition paramenters.

(b) Mass Spectroscopy. Mass spectra were taken with a Balzers QMS 311 quadrupolar mass spectrometer with a resolution (measured as $[m/\Delta m]$ at 10% peak height) of ≥ 180 for masses below 100. The gas flow into the ion source was regulated by means of a PFA needle valve (Young) in order to achieve a good signal to noise ratio while the excess gas was trapped on a cold shield (77 K) around the ion source. In this way, no background gas or decomposition products could be formed inside the mass spectrometer.

(c) UV Spectroscopy. UV spectra were recorded with a 1024 diode array spectrometer system (Spectroscopy International) using a CLD 30-W deuterium lamp (Hamamatsu) as a light source. Hg emission lines were used for wavelength calibration. Gas phase spectra were recorded in the transmission mode using a Duran glass cell (optical path length: 10 cm) equipped with quartz windows (Suprasil, Heraeus). Pressures were measured with a capacitance manometer (MKS Baratron 122 A, 10 mbar absolute). The monochromator and the housing of the absorption cell were flushed with N_2 to eliminate absorption from atmospheric O_2.

(d) Melting Point and Vapor Pressure. The melting point was determined inside a 6 mm glass tube using a Pt 100 resistance sensor (5 × 1 mm Heraeus).

Vapor pressures were measured with a capacitance manometer (MKS Baratron 122 A, 1000 mbar absolute) in the temperature range between 149 and 186 K.

Results and Discussion

During our studies, we recognized that the properties reported by Cauble and Cady[1] strongly depended on a particular impurity present in the samples. We confirmed that "even a single transfer of the product from trap to trap produces decomposition". However, it was also found that fluoroformyl hypofluorite free of this byproduct is stable for more than 8 h in the gas phase at about 100 mbar pressure and room temperature. The unstable byproduct is a little less volatile than FC(O)OF, and it decomposes to FC(O)F and O_2. The ^{19}F NMR spectrum shows two doublets of equal intensity at $\delta = 271.7$ and -31.3 ppm, $J(F,F) = 17.5$ Hz. Attempts to record some characteristic IR absorptions failed because its spectrum is very similar to that of FC(O)OF.

The chemical behavior and spectroscopic properties indicate that the unknown impurity most likely is FC(O)OOF. Referring to Table 1, the NMR signal at −31.3 ppm with a $J(^{13}C,F)$ coupling constant of 312 Hz is typical for a FC(O) group bonded to a very electronegative substituent, and the signal at 271.7 ppm is plausible for a OOF group. Going from XOF to XOOF compounds, the NMR resonance is shifted to higher frequencies in all instances (see Table 1).

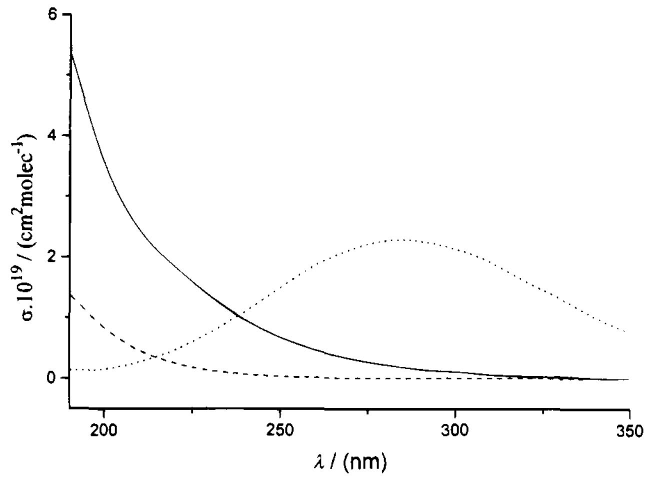

Figure 1. Gas phase UV spectra of FC(O)OOC(O)F (solid), FC(O)-OF (dashed), and $F_2 \times 10$ (dotted).

Removal of FC(O)OOF from FC(O)OF was finally achieved by thermal decomposition of the former in the gas phase and refractionation of the product mixture.

Physical and Spectroscopic Properties of FC(O)OF. Gaseous FC(O)OF condenses as a pale yellow liquid which has a melting point of 115 K. The boiling point extrapolated from the vapor pressure curve, $\log p = 8.723 - 1226.093)/T$ (p in mbar, T in K), recorded between 149 and 186 K is 214 K, compared to a previously reported value of 218 K.[1] Eighteen data points were taken between these two temperatures, and the correlation coefficient was better than 0.999. The higher melting point of 132 K reported by Cauble and Cady[1] is due to the impurity FC(O)OOF in their samples, which forms a solid solution with FC(O)OF.

In the UV region, FC(O)OF shows an unstructured continuous absorption (Figure 1) similar to that of the precursor FC(O)-OOC(O)F which can be assigned to a $\pi^* \leftarrow n$ transition. For comparison reasons, the UV spectrum of F_2 is also included.

The 70 eV mass spectrum of FC(O)OF shows the following fragment ions, m/z (%, ion): 63 (5.2, FCO_2^+), 47 (100, FCO^+), 44 (53.7, CO_2^+), 35 (9.7, OF^+), 32 (3.7, O_2^+), 31 (11.2, CF^+), 28 (64.9, CO^+), 19 (74.6, F^+), 16 (80.6, O^+), 12 (34.3, C^+). The fact that the base peak is FCO^+ is in accordance with the high stability of the cation (which is isoelectronic with FCN) and the weak C—OF bond. No parent peak was detected, which is also the case for other hypofluorites.[11] A detailed analysis of the vibrational spectra of FC(O)OF in the gaseous, liquid, and solid phases as well as isolated in inert gas matrices is described elsewhere.[12]

Investigation of the Equilibrium *cis*-FC(O)OF $\rightleftharpoons$ *trans*-FC(O)OF by ^{19}F NMR Spectroscopy. The FC(O)OF molecule is isoelectronic with the planar O_2NOF molecule,[13] and the F atoms can acquire two different orientations (eq 1).

Indeed the ^{19}F NMR spectrum of pure FC(O)OF shows at 183 K clearly two pairs of doublets at −38.1/−21.1 and 201.3/223.0 ppm with high/low intensity, repectively (Figure 2).[14] The species of higher abundance exhibits a $J(F,F)$ coupling constant of 173.3 Hz and the other of 17.7 Hz. Since in similar molecules the $J(F,F)$ *trans* coupling constants are always larger

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(14) In ref 1 only two signals for FC(O)OF at −37 and 209 ppm exhibiting a coupling constant of 141 Hz were reported. The differences may be due to differences in the measurement techniques.

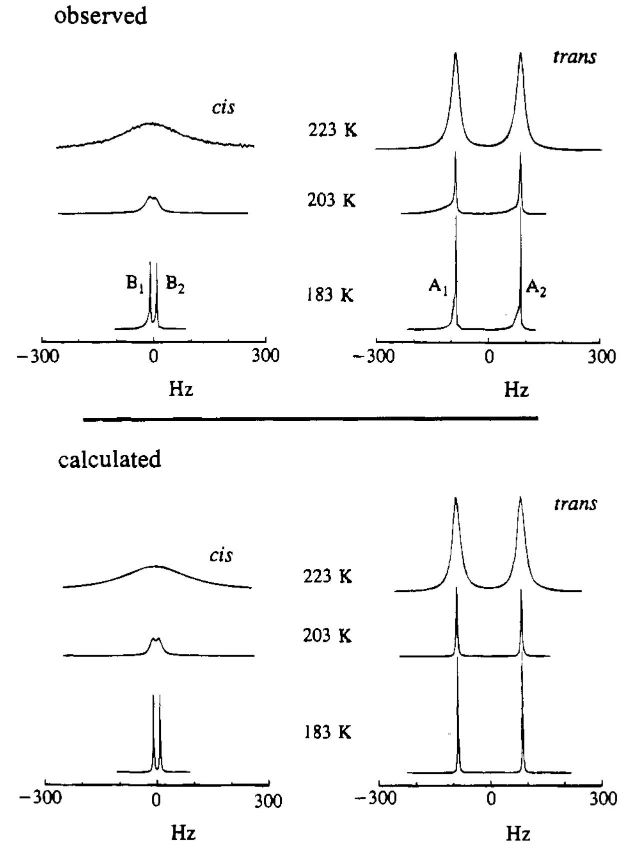


Figure 2. Temperature dependence of the ^{19}F NMR spectra of equilibrium mixtures of *cis* (B_1/B_2) and *trans* (A_1/A_2) FC(O)OF in the liquid phase. The signals in the FC(O) and OF regions are identical. The signals for *cis*-FC(O)OF are enlarged by a factor of 10.

than those for the *cis* conformers (e.g. N_2F_2 322/99, CF_2NF 184/23, and CHFCHF 133/19),[15] the resonances at −38.1 and 201.3 ppm are assigned to *trans*-FC(O)OF. Additionally, *trans*-FC(O)OF is characterized by the isotopic shifts $^1\Delta[^{19}F(^{13/12}C)] = -0.13$ and $^1\Delta[^{19}F(^{18/16}O)] = -0.62$ ppm.

With increasing temperatures, the signals of the more stable *trans* rotamer decreased and the interconversion equilibrium between the two conformations (eq 1) was studied by recording the line broadening of the ^{19}F NMR signals. The assignment that the *trans* rotamer is more stable than the *cis* rotamer is in accordance with our vibrational study.[12] Figures 2 and 3 show the changes in the features of the −OF signals (the same behavior is observed for the FC(O) signals) for liquid and gaseous FC(O)OF, respectively. In the gas phase at 298 K, the equilibrium mixture consists of 13 ± 2% *cis*- and 87 ± 2% *trans*-FC(O)OF. The $J(F,F)$ coupling is not resolved in the gas phase spectra because the natural line width is strongly increased by fast spin−lattice relaxation.

By use of a nonlinear least-squares fit, the two signals for *cis*- and *trans*-FC(O)OF were fitted to the line shape function $g(\nu)$.[16] The mean lifetimes of both conformers in the gas phase as well as in the liquid phase were fitted using their fixed line widths at 230 and 183 K, respectively, and their *cis*/*trans* molar ratios from the temperature dependence of the equilibrium constant.[12] In the liquid phase the spectra were simulated using the frequency differences $\nu_{A1} - \nu_{B1}$ and $\nu_{A2} - \nu_{B2}$ (Figure 2) of the resonance frequencies of the nuclei in *cis* and *trans* conformations. From 11 different experiments in the temperature range 230−360 K, the linear regression of the mean lifetimes of *cis*- and *trans*-FC(O)OF in the gas phase versus the reciprocal temperature leads to the Arrhenius parameters τ_∞ (s) = (11 ± 5) × 10^{-11}, (6 ± 3) × 10^{-11} and E_a (kJ mol^{-1}) = 35.0 ± 1.1, 40.4 ± 1.2 for *cis*-, *trans*-FC(O)OF, respectively.

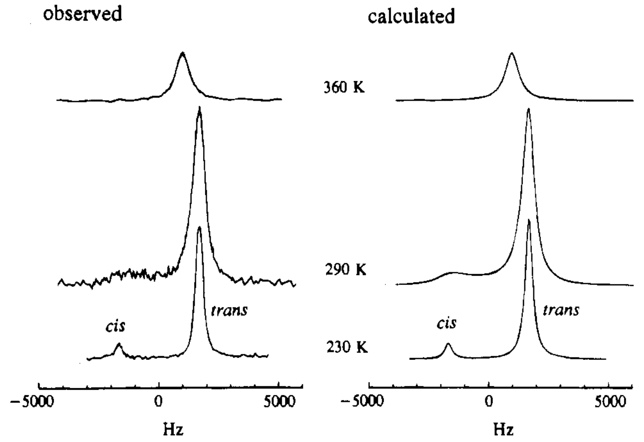
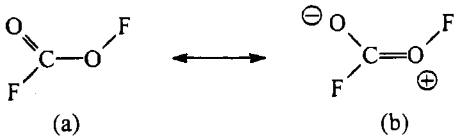


Figure 3. Temperature dependence of the ^{19}F NMR spectra of equilibrium mixtures of *cis*- and *trans*- FC(O)OF in the gas phase.

The observed barrier to internal rotation around the C−OF bond holds the molecule in the planar configuration. This can be rationalized by some double-bond character of the C−OF bond due to significant contribution of isomer b to the resonance hybrid (eq 2) or by interaction of the oxygen lone pairs with the C(O)F group.



(2)

Nearly the same barrier is calculated for CH_3ONO around the O−NO bond,[17] but in *N*,*N*-dimethylformamide the barrier is much higher[16] (88 kJ mol^{-1}). The difference between the rotational barriers of *cis*- and *trans*-FC(O)OF of 5.4 ± 2.3 kJ mol^{-1} represents the reaction enthalpy for eq 1. This value is in excellent agreement with 4.9 ± 0.3 kJ mol^{-1} found in our infrared analysis.[12]

Mechanism of Formation of FC(O)OF. As stated in the Experimental Section, we tried to prepare pure $FC(^{18}O)OF$ and $FC(O)^{18}OF$ from $C^{18}O$ and $^{18}O_2$, respectively. However, the IR and mass spectra of the final product showed the presence of a mixture of both isotopomers.

In order to clarify the mechanism of FC(O)OF formation, we carried out a mass spectroscopic study of the initial step in the synthesis of FC(O)OF, that is, the formation of bis(fluoroformyl) peroxide from a mixture of O_2, F_2, and CO.[18]

For bis(fluoroformyl) peroxide, the 70 eV mass spectrum shows all the relevant fragment ions, *m*/*z* (%, ion): 126 (3.3, M^+), 63 (17.4, FCO_2^+), 47 (100, FCO^+), 44 (37.4, CO_2^+), 32 (2.4, O_2^+), 31 (4.8, CF^+), 28 (20.3, CO^+), 19 (7.4, F^+), 16 (14.8, O^+), 12 (4.4, C^+).

For comparison, see ref 19, where CO_2^+ is reported as the most intense peak, possibly from CO_2 as the main impurity.

The FCO^+ and O_2^+ fragments can be used to follow the fate of the ^{18}O atoms. If they come from $C^{18}O$, the FCO^+ fragment

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should appear at $m/z = 49$, and when $^{18}O_2$ is used, the O_2^+ fragment should appear at $m/z = 36$. However, the mass spectra of FC(O)OOC(O)F from both ^{18}O sources proved to be very similar and in particular, the ions at $m/z = 47$ and 49 showed the same intensities and the ions at 32, 34, and 36 showed a 1/2/1 intensity ratio. These results show that the species FC(^{18}O)OOC(^{18}O)F, FC(^{18}O)O^{18}OC(O)F, and FC(O)^{18}O^{18}OC(O)F are present in a ratio of 1/2/1, respectively, and that the ^{18}O atoms are statistically distributed.

Aymonino et al.[18] postulated (3) as the only source of

$$FC(O)O_2 + FC(O)O_2 \rightarrow FC(O)OOC(O)F + O_2 \quad (3)$$

peroxide. Very recently, another channel for the self-reaction was proposed:[20]

$$2FC(O)O_2 \rightarrow 2\,FCO_2 + O_2 \quad (4a)$$

$$2FCO_2 \rightarrow FC(O)OOC(O)F \quad (4b)$$

The branching ratio (4/3) is given as 80 ± 20%, which is insufficient to explain the observed distribution of ^{18}O. Also recently, an equilibrium between the FC(O)O radicals and the peroxide was postulated.[21] This would be in agreement with the results of our experiments. The formation of FC(O)O radicals is needed in order to explain the statistical distribution of the ^{18}O atoms in our synthesis.

Photolysis of bis(fluoroformyl) peroxide in the presence of fluorine yields FC(O)OF besides CO_2, FC(O)F, CF_3OF, SiF_4, CF_3OOCF_3, $FC(O)OOCF_3$, and CF_3OOOCF_3.[1] In order to understand the mechanism of this second step in the synthesis of FC(O)OF, we studied the influence of (i) the wavelength of photolysis and (ii) the ratio of FC(O)OOC(O)F to F_2. UV radiation of 254 nm (low-pressure Hg lamp) gives higher yields of FC(O)OF and smaller amounts of byproducts than broad-band UV photolysis at >300 nm (high-pressure Hg lamp in combination with a glass vessel). The same was observed in the laboratory of DesMarteau.[22] Highest yields of FC(O)OF were observed with a FC(O)OOC(O)F/F_2 ratio of 1/1.

The mechanism of FC(O)OF formation can be rationalized on account of the primary process occurring in the photolysis (Figure 1) and the subsequent reactions. With light of $\lambda = 254$ nm mainly the peroxide and very little of the fluorine is photodissociated:

$$FC(O)OOC(O)F + h\nu \rightarrow 2FCO_2 \quad (5)$$

with a minor contribution from

$$FC(O)OOC(O)F + h\nu \rightarrow FC(O)O_2 + FC(O) \quad (6)$$

followed by

$$FC(O) + F_2 \rightarrow FC(O)F + F \quad (7)$$

$$FCO_2 + F_2 \rightarrow FC(O)OF + F \quad (8)$$

$$FC(O)O_2 + F_2 \rightarrow FC(O)OOF + F \quad (9)$$

$$FC(O)F + F \rightarrow F_3CO \quad (10)$$

and further fluorination reactions which explain the observed products. Conversely, for $\lambda > 300$ nm, the F atom concentration would be higher than the FCO_2 radical concentration especially with high F_2 partial pressure:

$$F_2 + h\nu \rightarrow 2F \quad (11)$$

Consequently, more perfluorinated products appear. Under these conditions, the product showed an increased formation in particular of F_3COOCF_3 and $FC(O)OOCF_3$. Thus, we propose that (5) and (8) are the crucial steps in the synthesis of FC(O)OF.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support and Solvay Hannover and MAN München—in particular Dr. E. Jacob—for the donation of fluorine and laboratory equipment, respectively. G.A.A. is indebted to the Alexander von Humboldt Stiftung for a fellowship.

IC940585W

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