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Reactions of poly-hexafluoropropylene oxide acids and their corresponding salts

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Abstract

Investigation of the decomposition or fluorination of poly-hexafluoropropylene oxide (poly-HFPO) carboxylic acids and their salts reveals a new type of product from the decarboxylation of poly-HFPO and proposes an explanation for its formation.

Keywords: Mechanism; Mass spectrometry; Perfluorinated ether

1. Introduction

Perfluorinated polyethers are an important class of compounds, functioning as chemically inert, high temperature lubricants and fluids and high temperature greases for corrosive environments. Since the discovery and application of Krytox® in the mid 1960s [1,2], other similar materials have been synthesized providing a rich literature of new and exciting chemistries.

The decarboxylation reaction of perfluorinated compounds has been little studied. One report in 1953 [3] describes the reaction of normal perfluoroalkyl carboxylic acids in basic, protic media, the products being carbon dioxide and the corresponding difluorohydro terminated perfluoroalkane. Poly-hexafluoropropylene oxide (poly-HFPO) carboxylic acids are reported to undergo similar reactions with the same results [4]. We have revisited the decarboxylation and fluorination of poly-HFPO carboxylic acids in an effort to better understand their chemistry.

2. Results

2.1. Decarboxylation

A mixture of low molecular weight poly-HFPO acid fluoride [5,6] was isolated and further fractionated using distillation to a very narrow cut. This material was then hydrolyzed to the acid with a portion converted to the corresponding ammonium salt. Decarboxylation experiments were undertaken by slowly raising the temperature of the specific materials until evolution of carbon dioxide was observed. The reaction mass was held at this temperature for 1 h at which time the CO_2 evolution ceased and the decomposition was determined to be complete (Table 1).

Decarboxylation reaction product analysis was first conducted with gas chromatographic–electron impact mass spectroscopy. This method yields one peak in the case of the carboxylate salt reactions, while the higher temperature decomposition of the free acid yields this same peak plus one additional peak (Fig. 1). The mass spectrum of both peaks shows the presence of hydrogen with the characteristic *m/e* of either 101 or 151. The large peak in both spectra shows the expected decomposition product with a $-CFHCF_3$ (HEC) terminal group. The other peak shows a new hydrogen-con-

Table 1
Decomposition data

	Decomposition temperature	Major product	Minor product
Pure acid	220°C	HEC[a]	IPA-H[b]
Pure ammonium salt	160°C	HEC	–
Acid/KOH/protic solvent	100°C	HEC	–

[a] HEC represents $F[CF(CF_3)CF_2O]_4CFHCF_3$.
[b] IPA-H represents $F[CF(CF_3)CF_2O]_4CF(CF_3)CF_2H$.

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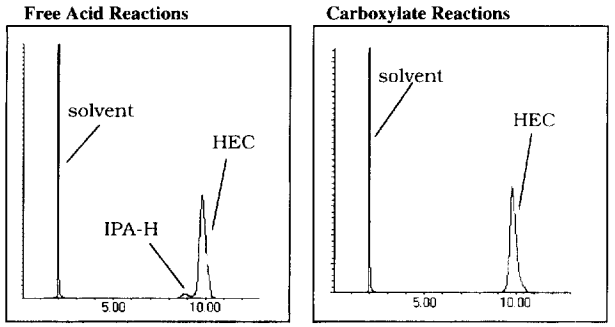
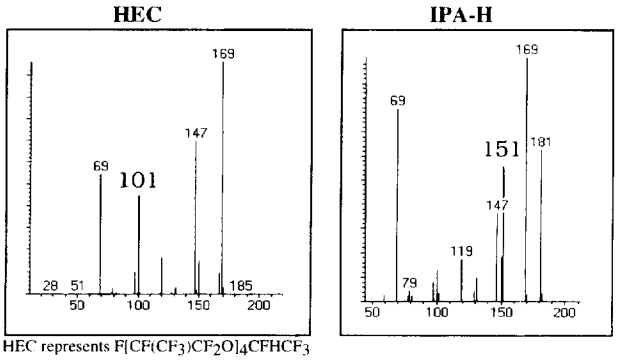


HEC represents F[CF(CF$_3$)CF$_2$O]$_4$CFHCF$_3$
IPA-H represents F[CF(CF$_3$)CF$_2$O]$_4$CF(CF$_3$)CF$_2$H

Fig. 1. Decomposition gas chromatograms.



HEC represents F[CF(CF$_3$)CF$_2$O]$_4$CFHCF$_3$
IPA-H represents F[CF(CF$_3$)CF$_2$O]$_4$CF(CF$_3$)CF$_2$H

Fig. 2. Decomposition mass spectra (EI).

taining polyether structure, subsequently identified as a compound containing a terminal $-CF(CF_3)CF_2H$ moiety (IPA-H) (Fig. 2).

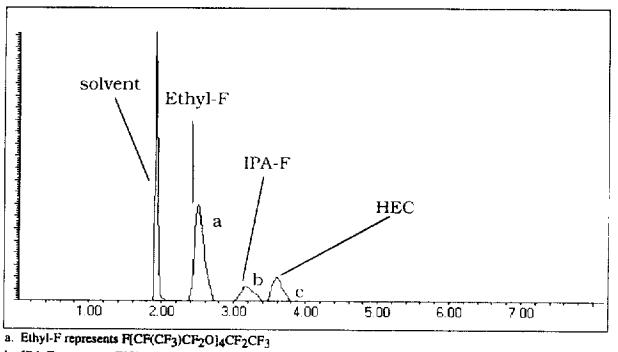
Gas chromatographic–chemical ionization mass spectrometry was used to further verify the identity of the GC peaks as HEC and IPA-H, showing the characteristic main ion peaks with *m/e* equal to $[M+H-HF]^+$ of 765 and 815, respectively.

2.2. Fluorination

As reported in Refs. [5,6], perfluorinated ethers are prepared by fluorinating the carboxylic acid with elemental fluorine at elevated temperatures (greater than 150°C).

Low molecular weight fractions of fluorinated poly-HFPO were fractionated and subjected to GC analysis. Three peaks (a, b and c) were identified using GC/EI/MS for each HFPO repeat unit (Fig. 3). Two of the peaks have mass spectra corresponding to perfluorinated ethers (*m/e* = 69, 147, 169) and one peak, labeled HEC, clearly contains hydrogen (*m/e* = 101, $CHFCF_3$). The only difference in the EI mass spectrum of the two perfluorinated ethers is the extremely reduced *m/e* 119 for the minor component, indicative of minimal amounts of CF_2CF_3 (Fig. 4).

GC/CI/MS permits the specific identification of peaks a and b as perfluoroethyl and perfluoroisopropyl terminated fluoroethers, respectively. As with the acid decomposition products, the CI mass spectrum is illustrative in showing



a. Ethyl-F represents F[CF(CF$_3$)CF$_2$O]$_4$CF$_2$CF$_3$
b. IPA-F represents F[CF(CF$_3$)CF$_2$O]$_4$CF(CF$_3$)$_2$
c. HEC represents F[CF(CF$_3$)CF$_2$O]$_4$CFHCF$_3$

Fig. 3. Fluorination gas chromatogram.

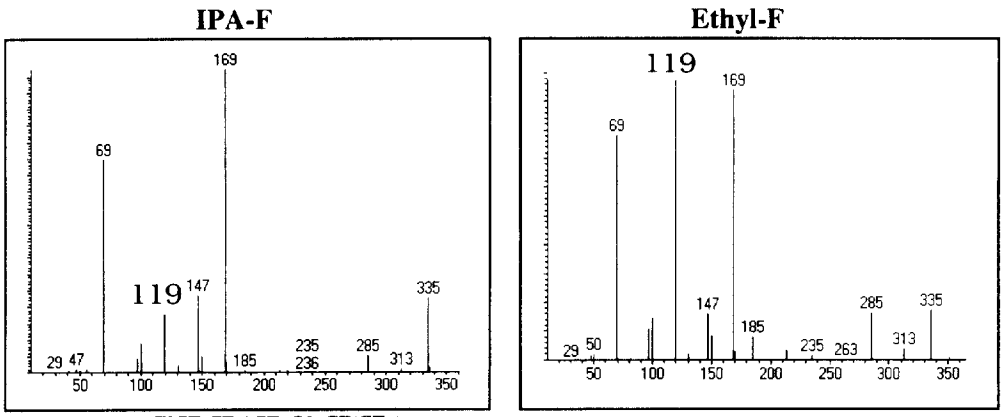
the difference between the isopropyl and ethyl groups, with a large characteristic peak at $[M+H-HF]^+$ 833 for $F[CF(CF_3)CF_2O]_4CF(CF_3)_2$ and 783 for $F[CF(CF_3)CF_2O]_4CF_2CF_3$ with a difference of one CF_2 unit (50 amu). Peak c is identical to the main product of the decomposition experiments with $[M+H-HF]^+$ of 765 for $F[CF(CF_3)CF_2O]_4CFHCF_3$ (HEC).

2.3. ^{13}C NMR

The structural proof for three of the proposed materials, Ethyl-F, IPA-F and HEC, is confirmed from an analysis of the ^{13}C NMR spectra of the three pure materials. The significant carbon atoms are numbered in Fig. 5 below.

All of the materials have a common *n*-propyl group produced by the initial HFPO ring opening. One would expect a quartet of triplets for the C(1) carbon—a large ^1J coupling to the three adjacent fluorines and a ^2J coupling to the two fluorines on C(2). Carbon (2) would be expected to be a triplet of quartets of triplets with one large ^1J and two smaller ^2J couplings. With carbon (3), one would expect a triplet of triplets with one large ^1J and one smaller ^2J coupling. Carbon (3) also displays a ^3J interaction with the fluorine atom bonded to the methine carbon in the adjacent repeat unit. The data show little to no variation due to different end groups: C(1) 118.6 ppm (q,t), $^1J = 284.1$–285.5 Hz, $^2J = 32.8$ Hz; C(2) 108.1 ppm (t,q,t), $^1J = 267.8$–268.0 Hz, $^2JCF_3 = 39.7$ Hz, $^2JCF_2 = 35.6$ Hz; and C(3) 117.1 ppm (t,t,d), $^1J = 287.3$–288.1 Hz, $^2J = 31.2$ Hz, $^3J = 4.6$ Hz.

The more significant carbon atoms are carbons (4) and (5) and their data are given in Table 2. For all of the compounds, the terminal C(5) carbon is straightforward, being a quartet of doublets or triplets, with large ^1J and smaller ^2J couplings. The chemical shift differences between the compounds is much larger here than for the other terminal *n*-propyl carbons. The analysis of the C(4) carbon speaker provides definitive proof of each structure. For the perfluoroethyl group, the expected triplet of quartets is found, with couplings of the same magnitude as before. For the perfluoroisopropyl terminal, a doublet of septets is found, as expected, again with reasonable ^1J and ^2J couplings. For the



IPA-F represents $F[CF(CF_3)CF_2O]_4CF(CF_3)_2$

Ethyl-F represents $F[CF(CF_3)CF_2O]_4CF_2CF_3$

Fig. 4. Fluorination mass spectra (EI).

$F_3C - C F_2 - CF_2O[CF(CF_3)CF_2O]_n - C X F - CF_3$

(1) (2) (3) (4) (5)

Fig. 5.

Table 2
^{13}C NMR spectral data for Ethyl-F, HEC and IPA-F poly-HFPO

	C(4)	C(5)
Ethyl ($n=4$, $X=F$)		
δ [ppm]	117.9 (t,q)	115.6 (q,t)
^1J [Hz]	283.7	286.5
^2J [Hz]	40.6	44.4
HEC ($n=4$, $X=H$)		
δ [ppm]	97.85 (d,d,q,t)	119.6 (q,d)
^1J [Hz]	244.8/181.9	279.7
^2J [Hz]	42.9	31.1
^3J [Hz]	5.3	
IPA ($n=5$, $X=CF_3$)		
δ [ppm]	103.6 (d,sept)	119.2 (q,d)
^1J [Hz]	268.3	287.0
^2J [Hz]	39.1	30.8

HEC derivative, one finds a doublet of doublets of quartets of triplets, with the doublet of doublets arising from the carbon–fluorine and carbon–hydrogen couplings. Secondary coupling to the adjacent carbon fluorines gives the expected quartet splitting in the same range as the other compounds. The very small ^3J coupling observed, being a triplet, must result from a long range interaction with the adjacent ether methylene fluorine atoms.

3. Discussion

The discovery of both an isopropyl group containing one hydrogen from the decarboxylation of the free acid and a perfluorinated isopropyl group in the fluorinated poly-HFPO is prima facie evidence for a β-scission reaction following loss of carbon dioxide in either decarboxylation or fluorination. Whether this reaction is radical (Scheme 1) or ionic (Scheme 2) in nature was not determined, however, because both reactions were done at elevated temperatures, it is believed that these reactions have a radical component. The lower temperature and absence of β-scission reactions in the salt decarboxylations are consistent with an ionic mechanism.

Scheme 1A begins with the homolytic cleavage of the O–H bond of the carboxylic acid followed by loss of carbon dioxide. The resulting poly-HFPO carbon radical may either capture a hydrogen atom giving predominately HEC, or undergo a β-scission to give the radical ending in $CF_2^{\bullet}$ and trifluoroacetyl fluoride. The IPA radical can then capture a hydrogen atom giving the observed IPA-H.

Scheme 1B begins with the fluorination of the carboxylic acid by elemental fluorine giving the carboxylate radical, possibly through the formyl hypofluorite intermediate (step 2). Following decarboxylation three different routes are possible: (1) fluorination by elemental fluorine or a fluorine atom producing the perfluoroethyl terminated molecule, (2) the radical may capture a hydrogen atom from HF or –COOH giving HEC, or (3) the radical can undergo a β-scission to give the new radical ending in $CF_2^{\bullet}$ and trifluoroacetyl fluoride. This radical ending in $CF_2^{\bullet}$ may then capture either a fluorine or hydrogen atom to form IPA-F or IPA-H, respectively, with the latter not being observed. The absence of IPA-H in the fluorination is undoubtedly due to the low concentration of both the radical ending in $CF_2^{\bullet}$ and hydrogen atoms. The presence of the IPA-F is confirmatory evidence of the β-scission pathway.

Scheme 2 starts with the carboxylate salt of the carboxylic acid. This salt then decarboxylates apparently to the poly-HFPO anion which might either abstract a proton from the solvent giving HEC, or undergo a β-scission to give the anion ending in CF_2^- and trifluoroacetyl fluoride. IPA-H could be formed by subsequent abstraction of a solvent proton. However, in the case of both the ammonium and potassium salts, this product was not observed. The absence of the IPA-H, which is consistent with an ionic mechanism, can be attributed to the low reaction temperature and large molar excess of protons.

Step 1: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COOH$ -----> (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COO\bullet$ + H•

Step 2: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COO\bullet$ -----> (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ + CO_2

Step 3: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ + H• -----> (pHFPO)-$OCF(CF_3)CF_2OCFHCF_3$ (HEC)

Step 4: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ -----> (pHFPO)-$OCF(CF_3)CF_2\bullet$ + CF_3COF (ß-scission)

Step 5: (pHFPO)-$OCF(CF_3)CF_2\bullet$ + H• -----> (pHFPO)-$OCF(CF_3)CF_2H$ (IPA-H)

(pHFPO)- = $F[CF(CF_3)CF_2O]_n$-

(a)

Step 1: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COOH$ + F_2 -----> (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COOF$ + HF

Step 2: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COOF$ -----> (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COO\bullet$ + F•

Step 3: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)COO\bullet$ -----> (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ + CO_2

Step 4: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ + F_2/F• -----> (pHFPO)-$OCF(CF_3)CF_2OCF_2CF_3$ (Ethyl-F) + F•

Step 5: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ + HF/-COOH -----> (pHFPO)-$OCF(CF_3)CF_2OCFHCF_3$ (HEC) + F•

Step 6: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)\bullet$ -----> (pHFPO)-$OCF(CF_3)CF_2\bullet$ + CF_3COF (ß-scission)

Step 7: (pHFPO)-$OCF(CF_3)CF_2\bullet$ + F_2/F• -----> (pHFPO)-$OCF(CF_3)_2$ + F• (IPA-F)

Step 8: (pHFPO)-$OCF(CF_3)CF_2\bullet$ + HF/-COOH -----> (pHFPO)-$OCF(CF_3)CF_2H$ + F• (IPA-H, not observed)

(b)

Scheme 1. (A) Radical decarboxylation mechanism of free acid. (B) Radical fluorination of free acid.

Step 1: (pHFPO)-$OCF(CF_3)COO^-M^+$ + Heat -----> (pHFPO)-$OCF(CF_3)^-M^+$ + CO_2

Step 2: (pHFPO)-$OCF(CF_3)^-M^+$ + HX -----> (pHFPO)-$OCFHCF_3$ + MX (HEC)

Step 3: (pHFPO)-$OCF(CF_3)CF_2OCF(CF_3)^-M^+$ -----> (pHFPO)-$OCF(CF_3)CF_2^-M^+$ + CF_3COF (ß-scission)

Step 4: (pHFPO)-$OCF(CF_3)CF_2^-M^+$ + HX -----> (pHFPO)-$OCF(CF_3)CF_2H$ (IPA-H, not observed) + MX

Scheme 2. Ionic decarboxylation.

4. Conclusions

Although the chemistry of perfluoropolyethers is well known and extensively studied, this investigation demonstrates new types of products from the decarboxylation of poly-HFPO acid (IPA-H, IPA-F) and proposes an explanation for their formation. These secondary products appear to be the result of radical reactions following the unexpected β-scission. No comparable examples of this chemistry with the corresponding hydrocarbon analogs are reported.

5. Experimental

A fraction of low molecular weight poly-HFPO acid fluoride was obtained from cesium fluoride catalyzed polymerization of HFPO [5] and distilled to a narrow molecular weight distribution. Following hydrolysis, this product was fluorinated as described in Ref. [6] and a low molecular weight cut was isolated. Other chemical reagents were commercially available and used as received.

Gas chromatographic/mass spectrometric data were obtained using a Hewlett Packard HP 5890 Series II gas chromatograph with a Series 5970 mass selective detector. Unless otherwise reported, yields obtained are estimated. Chemical ionization mass spectra were taken on an HP 5989B mass spectrometer. The reaction was monitored with a HP 5890 GC using a 30 m DB-1 column with a 2 min hold at 60°C and then taken to 200°C at 10°C min^{-1}. The flow rate was 1.59 cm^3 min^{-1} and splitless. Infrared spectra were obtained on a Nicolet 730 or 740 FT-IR Spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM360 using neat 5 mm samples with a trace of $CHCl_3$ for shimming and as a ^{13}C reference ($\delta CHCl_3 = 77.0$ ppm).

5.1. Preparation of poly-HFPO acid

As described in US Patent 3,367,868 [7]—in a typical reaction, a 500-ml three-necked Pyrex glass reactor was equipped with a magnetic agitator, a thermocouple, a reflux condenser and an additional funnel. The reactor was charged with 250 g (0.188 moles) poly-HFPO acid fluoride followed by the slow addition of 250 g (30 wt.%) aqueous calcium

chloride. The reaction mixture was held at room temperature (15–25°C) for 1 h and then 50°C for 1 h. The product was extracted with 100 ml Freon-113 and washed three times with a 10% acetone, 1% NaCl aqueous solution to break emulsions. The product was dried over magnesium sulfate and the solvent removed under reduced pressure. Typical yields were 90–95%. IR data are given in Table 3.

5.2. Preparation of poly-HFPO ammonium salt

As described in US Patent 3,367,868 [7]—in a typical reaction, a 250-ml three-necked Pyrex glass reactor was equipped with a magnetic agitator, a thermocouple, a dry ice condenser and an additional funnel. The reactor was charged with 100 g (0.075 moles) poly-HFPO acid and 100 ml Freon-113. While the reaction mass was held at 0–10°C, anhydrous ammonia was bubbled in slowly until the reaction mixture tested basic. The reaction mixture was then warmed to room temperature (15–25°C) and held for 1 h. Solvent was removed under reduced pressure yielding a brown wax. Typical yields were 85–90%. IR data are given in Table 3.

5.3. Poly-HFPO acid decomposition

In a typical reaction, a 10-ml two-necked Pyrex glass reactor was equipped with a magnetic agitator, a thermocouple and a reflux condenser. The reactor was charged with 10 g (7.5 mmol) poly-HFPO acid and heated slowly to 220°C for 1 h. After 1 h, the reaction was cooled to room temperature and the contents of the reaction vessel analyzed. GC results of the pot residue (ca. 9.2 g) indicate the sample to be ca. 96% HEC and 4% IPA-H (Figs. 1 and 2, Tables 1 and 4).

5.4. Poly-HFPO ammonium salt decomposition

In a typical reaction, a 10-ml two-necked Pyrex glass reactor was equipped with a magnetic agitator, a thermocouple and a reflux condenser. The reactor was charged with 10 g (7.5 mmol) poly-HFPO ammonium salt and heated slowly to 160°C for 1 h. After 1 h, the reaction was cooled to room temperature and the contents of the reaction vessel analyzed. GC results of the pot residue (ca. 8.4 g) indicate the sample to be ca. 100% HEC (Figs. 1 and 2, Tables 1 and 4).

5.5. Poly-HFPO potassium salt decomposition

In a typical reaction, a 50-ml two-necked Pyrex glass reactor was equipped with a magnetic agitator, a thermocouple and a reflux condenser. The reactor was charged with 10 g (7.5 mmol) poly-HFPO acid, 0.30 g (5.4 mmol) potassium hydroxide and 20 ml ethylene glycol and heated slowly to 100°C for 1 h. After 1 h, the reaction was cooled to room temperature and the contents of the reaction vessel analyzed. GC results of the bottom layer of the pot residue (ca. 7.4 g) indicate the sample to be ca. 100% HEC (Figs. 1 and 2, Tables 1 and 4).

Table 3
IR spectral data

Absorbance (cm^{-1})	Intensity	Shape	Assignment
Acid			
1780	medium	sharp	carbonyl
Ammonium salt			
3600–2600	weak	broad	NH stretching
1650	sharp	sharp	carbonyl
1520	weak	broad	CNH bending

Table 4
EI mass spectral data (relative intensities)

m/e	Ion	HEC	IPA-H	IPA-F	Ethyl-F
69	CF_3	53.3	80.4	68.5	66.8
97	C_2F_3O	10.4	6.6	–	13.6
100	C_2F_4	11.4	15.6	9.7	13.0
101	C_2F_4H	44.7	–	–	–
119	C_2F_5	15.5	17.6	15.7	89.0
131	C_3F_5	–	12.5	–	–
147	C_3F_5O	66.1	41.7	39.5	25.8
150	C_3F_6	13.9	15.8	8.6	13.3
151	C_3F_6H	–	53.8	–	–
167	C_3F_6HO	9.2	–	–	–
169	C_3F_7	100.0	100.0	100.0	100.0
181	C_4F_7	–	62.4	–	–
185	C_3F_7O	–	–	–	7.2
235	C_4F_9O	–	–	5.8	–
267	$C_5F_{10}HO$	31.5	–	–	–
285	$C_5F_{11}O$	17.5	9.0	5.8	26.6
313	$C_6F_{11}O_2$	8.5	–	–	6.0
317	$C_5F_{11}O_3$	–	7.6	–	–
335	$C_6F_{13}O$	30.1	22.7	31.3	22.9

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