Effects of Ultrasounds on Neat Nitrobenzene

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Neat nitrobenzene was continuously irradiated at two ultrasonic frequencies: 40 and 200 kHz, under air and argon atmosphere, respectively. Samples taken at intervals of 1, 5, 10 and 24 h were analyzed by GC-MS and decomposition products were identified. Possible reaction mechanisms are discussed. Presence of air as dissolved gas leads to oxygenated compounds such as 1,4-benzoquinone, 2,4-dinitrophenol, m-dinitrobenzene while argon inhibits the decomposition of nitrobenzene, especially at sonication times under 5 h. Based on the nature of the compounds identified we advanced a mechanism, involving a divergent splitting of unstable radical cation of NB in air and argon respectively. Thus, under air, the phenyl cation formation is preferred leading to 1,4-benzoquinone nitro-biphenyls and dinitrobenzene, while under argon, the phenyl radical formation seems to be favored, leading to phenol and diphenyl ether. The oxygenated compounds detected under argon clearly are a consequence of the nitro group splitting.

Keywords: ultrasound, nitrobenzene, frequency effect, mechanism

Nitrobenzene (NB) is cited by A. I. Vogel in his book Practical Organic Chemistry [1], as an extremely versatile solvent, and may frequently be employed for the crystallization of compounds which do not dissolve appreciably in the common organic solvents. In recent time two almost identical encyclopaedic books [2, 3] mentioned nitrobenzene used, sometimes as a solvent, in the manufacture of dyes, polishes, paints, drugs, pesticides, and synthetic rubber. In order to avoid artefacts caused by the effect of ultrasounds on organic compounds used as solvents, studies regarding their behavior in pure state under ultrasonic irradiation is very important.

Nitrobenzene received attention from sonochemists, some years ago, mainly due the colour change during sonication, indicating a chemical modification [4, 5]. The authors suggest that NB cleave into phenyl and NO_2 radicals, leading to further combination of aromatic rings, having as consequence a kind of polymerization [4-6]. The level of darkening was associated with the degree of polymerization and the influence of several factors such as type of bubbled gas, or addition of solutes was studied. It was found that the nature of bubbled gas has a major influence on the reaction rate with a more accentuated darkening in the presence of argon as compared with air. The rate of darkening is decreased when NB is diluted with benzene. The polymerization is attenuated in the presence of liquid solutes such as methanol, ethanol, 1-propanol, assumed as effective radical scavengers [6].

The authors stated that the radicals formed from the decomposition of NB are stable long enough to survive the collapse of cavitation bubble and initiate polymerization [7]. This characteristic is due to extension of π conjugation of benzene ring.

However, there are no data related to the nature of the products arising from sonication of nitrobenzene. Several papers describe the changes in electrical conductivity of sonicated organic liquids [8-11], fact observed and demonstrated in our group for nitrobenzene [12, 13]. Our interpretation for conductivity change and decomposition of NB was via self-electron transfer generating a pair of radical ions, which we think that are responsible for further reactions. Since we used nitrobenzene as solvent in our work we were interested to see if some of the compounds identified are artefacts coming from nitrobenzene sonication alone. In this study we report the results of sonication of neat nitrobenzene at two different frequencies 40 and 200 kHz. The resulting compounds were analysed and identified via GC-MS and a reaction mechanism, to account for these compounds, is proposed.

Experimental part

Materials

Nitrobenzene (99.90 %) purchased from Wako Chemicals was further purified by steam distillation, separation, dried on calcium chloride and each 12 h heated at 100°C for 10 min over 48 h time interval. After that, was distilled at atmospheric pressure and the fraction having the boiling point 210°C was collected. A GC-MS analysis of nitrobenzene was performed before use in order to detect traces of impurities and none were identified.

Method

A sample of 100 mL pure nitrobenzene was sonicated in 150 mL cylindrical glass vessel equipped with a side arm and a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. Two different frequencies (40 kHz and 200 kHz) were investigated. The sonications at 40 kHz were carried out in a Honda Electronics Ultrasonic Cleaner WS 1200-40 cleaning bath having maximum input power of 1200 watts. The power level was adjusted at 60% and no effective power determination was made. The reactions at 200 kHz were performed using a Kaijo Denki multi-wave ultrasonic generator Model 4021, having a 65 mm diameter barium titanate oscillator, with an input power of 200W. The temperature was maintained constant at 25±1°C for both types of frequencies by a stream of cold water. The sonication was carried out continuously for 24 h. One experimental setup was performed in the presence of atmospheric air, and another one in the presence of argon as protective gas. For the experimental setup under argon

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before ultrasonic irradiation the solution was purged with argon gas for 30 min at a constant flow rate of 5 mL/min, after the vessel being closed. During sampling, a flow of argon (same rate as above) was used to shield the solution from air contact.

Analysis

Samples of about 0.5 mL were withdrawn at 1, 5, 10 and 24 h and analyzed using a Shimadzu GC-MS Model QP-2010, equipped with a DB-1ms capillary column (0.25 mm x 30 m) J&W Scientific. In order to avoid the saturation of the MS detector with NB ions and to detect tiny amounts of NB sonodegradation, each sample was analyzed in two steps: first step for light components eluting in front of NB peak; second step for heavy components eluting after NB peak. NB is having 12 min retention time in our analytical conditions.

For the detection of light compounds, 1μL of sample was injected under the following conditions: the carrier gas was helium, the injector temperature was 250°C with a split ratio of 1:200 and the temperature of the detector was 300°C. Oven temperature started at 50°C for 3 min , increased at 250°C at a rate of 10°C /min and held for 10 mn. No solvent delay employed, and total running time was only 10 min.

For the detection of heavy compounds, 1μL of sample was injected under the following conditions: the carrier gas was helium, the injector temperature was 250°C with a split ratio of 1:50 and the temperature of the detector was 300°C. Oven temperature started at 50°C for 3 min , increased at 150°C at a rate of 15°C/min and held for 1 min, then increased to 300°C with a rate of 15°C /min and held for 10 min. The solvent delay time was 12.5 min and total running time was 30 min. In this way the NB was avoided entering the MS detector and therefore saturation of MS detector with nitrobenzene ions was eluded.

Data acquisition was carried out in scan mode (scanning from *m/z* 35 to *m/z* 500). The identification of the products was based on a comparison with NIST 107 and NIST 98 library spectra. For the light fraction, the benzene peak area value after 1 h sonication was taken as unit to which all other components were itemized. For heavy fraction the peak area of biphenyl was considered unit, and all other components were referred to it. The reason of this selection was that both compounds are hydrocarbons.

The peak areas of other compounds were divided to the corresponding unit peak area and the relative amount of products were obtained as a ratio. As the goal of this work was to determine the stability of NB under sonication, the compounds detected were regarded qualitatively. No quantitative determinations were performed.

Results and discussions

The reactions that take place under ultrasonic irradiation are well documented as the consequence of formation and collapse of cavitation bubbles [2, 14]. During their development, the cavitation bubbles entrap dissolved gas and vapours. At collapse, high temperatures and pressures are developed (over 5,000°K and over 2,000 atm) [15, 16], the result being homolytical breakage of chemical bonds. Therefore, reactive radical species are created, that further react, either with the entrapped gas, with the solvent or other reactive species.

In a previous work [12, 13] we reported that nitrobenzene changes its conductivity under sonication (fig. 1). Highly purified nitrobenzene (initial conductivity being under 0.01 μS/cm was sonicated for one hour at 40 kHz (Langford Sonomatic T175 ultrasonic cleaning bath), in a flat bottom glass vessel. The conductivity was measured using a Metrohm device equipped with a conductometric cell having the constant k = 0.675 cm^{-1}. To avoid the destruction of black platinum from the cell electrodes, the measurements were made with the ultrasound switched off at each 10 min time interval, followed by immersing the conductometric cell in NB and the conductivity recorded. After one hour the ultrasound was switched off and the conductivity was monitored continuously for an additional hour. As it is shown in the figure 1 at the end of two hours the conductivity reached a new plateau value higher than the initial one.

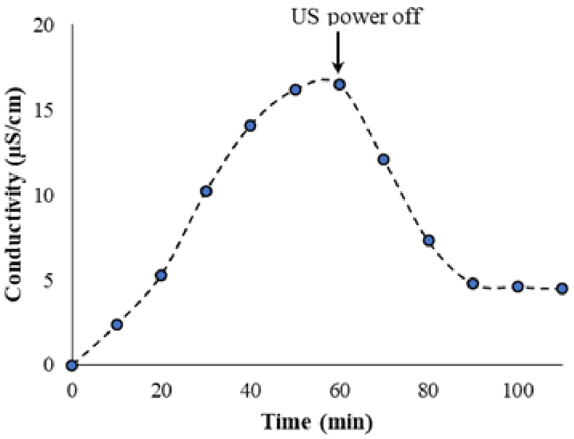


Fig. 1. Conductometric evolution for sonicated nitrobenzene.

This residual conductivity is a consequence of sonochemical changes of nitrobenzene and we interpreted this behavior via electron transfer mechanism (scheme 1):

$$PhNO_2 + PhNO_2 \xrightarrow{))))} \left.PhNO_2\right]^{+\cdot} + \left.PhNO_2\right]^{-\cdot} \qquad (1)$$

While analyzing the outcome of neat NB ultrasonic irradiation there are two directions to follow the discussion:

-one is the difference of products due to the presence of dissolved gas: air versus argon;

-another direction is to compare the products resulted from sonication at two different frequencies: 40kHz vs. 200kHz.

Influence of dissolved gas

Dissolved gases are part of the factors affecting the ultrasonic irradiation of liquids [17]. The temperature inside the collapsing cavitation bubble depends on the entrapped gas. The temperature decreases with the decrease in polytropic ratio (C_p/C_v) of the gas and increase with thermal conductivity. Therefore, the formation of reactive species is closely related to the nature of the dissolved gas. The polytropic ratio of argon is 1.66 while the polytropic ratio of air is 1.40; also, the thermal conductivity of air (0.0262 W/m*K) is higher than argon's thermal conductivity (0.016 W/m*K) [18, 19]. From these facts we can assume that when the sonication is conducted in the presence of air, the temperature in the cavitation bubble is lower than in the case of argon. That would lead to different distribution of intermediates and products.

When analyzing the light fraction compounds, only three compounds eluted in front of NB: benzene, phenol and 1,4-benzoquinone as result of NB sonication conditions (under air figure 2 or under argon figure 3). Benzene was selected as reference for light compounds fractions.

The most notable difference is that under air after 5 h of sonication 1,4-benzoquinone is detected, while under argon atmosphere only phenol is spotted and that just for 40 kHz frequency. These results are showing without any doubt that air is playing a role in NB sonication.

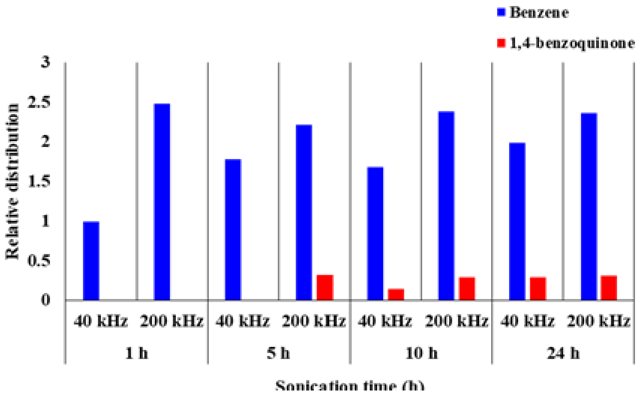


Fig. 2. Light compounds resulted from NB sonication under air

Argon is an inert gas, and its influence on the sonolysis is only a physical one (i.e. high temperature during the collapse of cavitation bubble). Air consists of reactive gases (oxygen) that can interfere/react with reactive species within liquid or can initiate a radical reaction. Higher amounts of compounds (in terms of peak area) were detected in the presence of dissolved air by comparison with dissolved argon.

Benzene was present as a product of NB sonication regardless the experimental conditions. Under air atmosphere the concentration of benzene is higher than in the case of argon. At 40 kHz, under air, the amount of benzene increases with sonication time, while under argon its concentration is constant with just a slight decrease towards 24 h sonication. Benzene accumulation occurs only after 10 h of sonication at 200 kHz under argon, slightly decreasing towards the end of sonication time.

The heavy components, after NB peak are shown in the figures 4 under air and 5 under argon. Biphenyl was selected as reference compound similarly as for benzene. Under air and 40 kHz biphenyl is detected after 5 h of sonication, while under argon it is present from the very beginning.

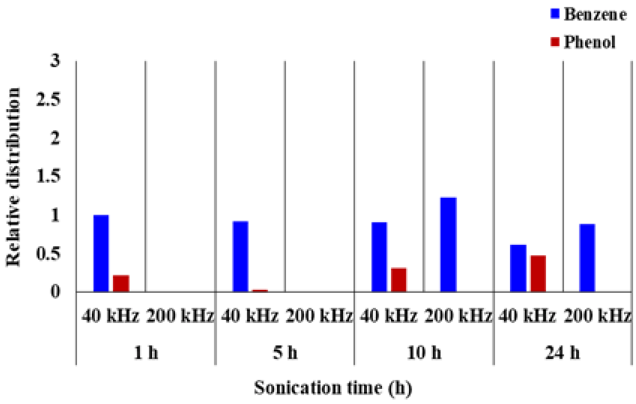
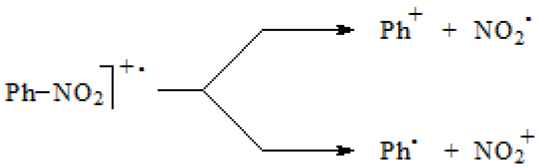


Fig. 3. Light compounds resulted from NB sonication under argon

We propose a mechanism having as first step scheme 1 that may account for both the conductometric changes during sonication and detected compounds. The second step consists in the splitting of unstable radical cation of NB according to scheme 2:



(2)

The unstable radical cation of NB can decompose in two ways:

a)Formation of phenyl cation and nitro radical- upper branch in scheme 2. This pathway is favored by the presence of air in the system.

b)Formation of phenyl radical and nitro cation- lower branch in scheme 2. This pathway is favored by the presence of argon in the solution.

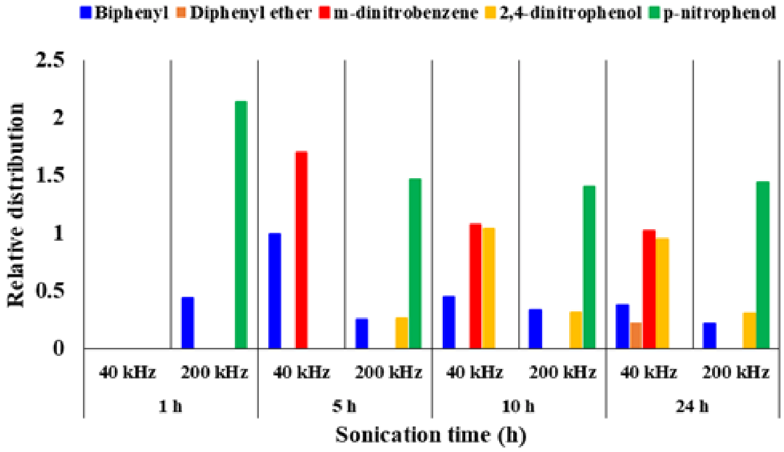


Fig. 4. Heavy compounds from NB sonication under air

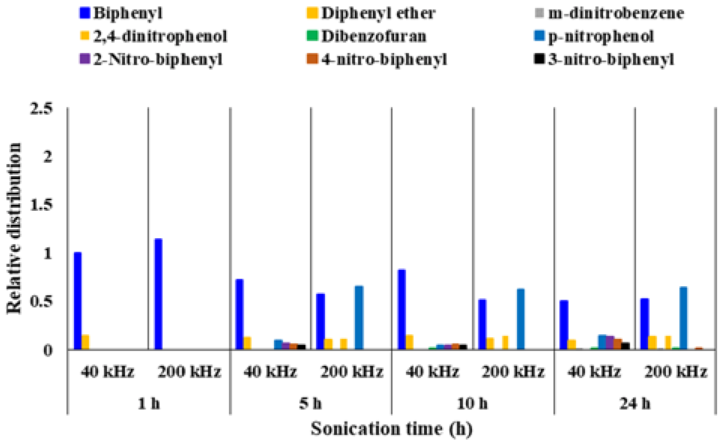
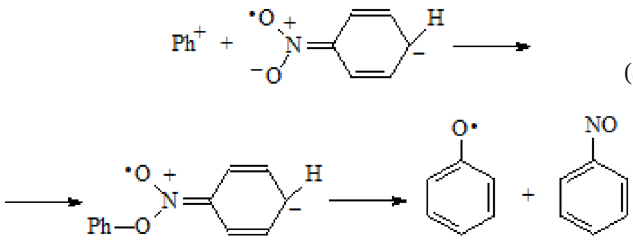


Fig. 5. Heavy compounds from NB sonication under argon

Some facts that lead toward this assumption is the absence of phenol under argon at 200 kHz, and presence of biphenyl from the beginning of sonication. This compound clearly results from phenyl radical dimerization.

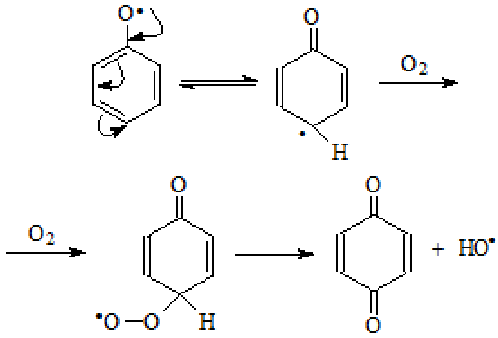
However, each pathway from scheme 2 is favored by the presence of one type of gas or the other. It does not occur unaccompanied. Both pathways are possible and may have different reaction rate under one or other gas. We can conclude that argon inhibits, in some extend, NB splitting via upper branch of scheme 2, fact obviously proved by biphenyl presence from the beginning of sonication.

Phenyl cation resulted from scheme 2 could react with nitrobenzene radical anion giving phenoxy radical and nitrozobenzene (scheme 3):



(3)

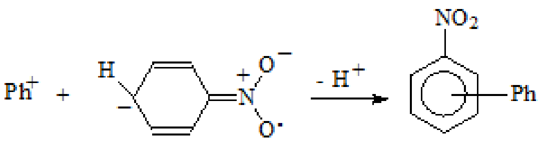
Phenoxy radical could trap oxygen from air resulting 1,4-benzoquinone (scheme 4):



(4)

Previous reports propose 1,4-benzoquinone formation as result of HO radical reaction with phenol, when phenol was sonicated in water solution [20]. In present experiments the water was absent, thus, the only way to obtain an oxygenated compound is either from phenyl radical reaction (resulting from NB homolytic cleavage) with oxygen from air or by a different reaction in which oxygen comes from NO_2 group of NB, fact confirmed by oxygenated compounds found under argon sonication (phenol and nitro-phenols).

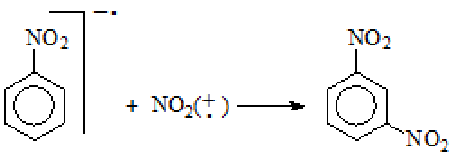
All nitro-biphenyls could be explained as result of the scheme 5 below:



(5)

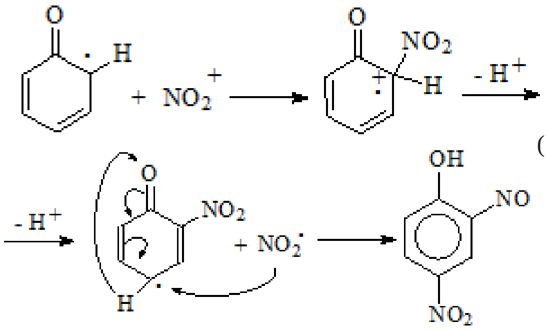
o,m,p-nitrobiphenyls

We can foresee the ongoing of the degradation as time passes: most of phenyl groups are coupling into polymeric chains, while the nitro group is captured by a molecule of nitrobenzene, either as radical or as cation leading to *m*-dinitrobenzene (scheme 6):



(6)

or by a nitrophenol intermediate (scheme 7):



(7)

When the NB radical cation splits into phenyl radical and NO_2 cation (scheme 2) the phenyl radical could extract a hydrogen atom from bulk NB resulting benzene and another NB radical cation (a kind of chain reaction). This reaction seems to be more favored under air atmosphere than under argon especially at higher frequency. Indubitably the benzene formation via a homolytic split of NB as effect of bubbles collapse could be explained as above [4-7, 21, 22], but in the absence of air it is hard to explain any oxygenated compounds. Also, the homolytic split does not account for conductivity change that couldn't return to the initial value after stopping sonication.

The NB's radical anion is more stable and does not suffers splitting. This radical anion is similar with those of NB reduction with metals [23]. However, this radical anion could react with other reactive species ultrasonically generated, leading therefore to the NB sonodegradation products, like nitrozobenzene, di-nitrobenzene and nitrobiphenyls. When comparing the NB degradation products in air versus argon, there is a narrow range of compounds detectable in case of air.

Influence of frequencies

There is not useful to discuss the NB sonodecomposition products taking into account only dissolved gas. Therefore, the following discussion will connect both dissolved gas and ultrasonic frequencies.

Another evident difference is a divergent distribution of products between 40kHz and 200kHz, especially on heavy components. Under air, at 40 kHz NB is degraded slowly and gradually, with biphenyl and *m*-dinitrobenzene detectable only after 5 h of irradiation. At 200 kHz, decomposition of nitrobenzene takes place faster: diphenyl and nitrophenol being detected after the first hour of irradiation. Interesting is the fact that *m*-dinitrobenzene is detected in traces under argon at 200kHz, suggesting a different mechanism under argon versus air, mechanism to which we advance the dissimilar splitting of NB radical cation explanation, formation of phenyl cation and nitro radical being favored under argon and higher frequency.

We made an experiment in which NB was sonicated at 40 kHz for 100 h (air atmosphere) and we were able to isolate a black solid material which melt over 400°C and burn without residue. This may be considered as a polymerization outcome of sonicated NB as mentioned in literature [4-6]. In order to account for the residual conductivity of sonicated NB, we performed a similar experiment as above and then washed the sonicated NB with distilled water (3 times with 25 mL). The water solution was found to be acidic, nitrous acid (0.005 moles in one mole of NB), which account for residual conductivity. To prove the nature of this acidic compound we try to induce diazotation of *p*-nitroaniline. Then we made a coupling reaction with β-naphthol. The resulting compound prove to be para red dye, figure 6, identical with those

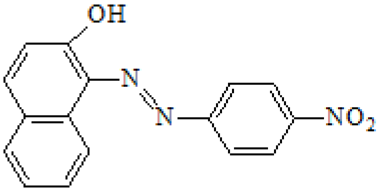


Fig. 6. Para red

prepared from pure compounds. This confirm without doubt that NB sonication produce nitrous acid [24] that account for residual conductivity.

Benzene formation cannot simply have explained without taking into account the solid material formation which could be a source of hydrogen which could react with phenyl radical formed via lower branch of scheme 2. However, it was found in higher amount at 200 kHz, denoting a higher influence of higher frequency on NB sonolytical decomposition. Diphenylether was detected in the presence of argon, while in the presence of air it was detected after 24 h of sonication only in traces at 40 kHz. This is a proof that in the absence of air, the oxygen atom in diphenylether is without doubt coming from the nitro group, otherwise it should be present in larger amounts. Thus, it can be assumed that was formed from phenoxy radical by reaction with another phenyl radical, confirming once again the fact that the presence of air as gas and lower frequency (40 kHz) favors the formation of phenyl cation and nitro radical.

Conclusions

The main conclusion of this study is that neat nitrobenzene suffers decomposition under ultrasonic irradiation, generating compounds that could lead to possible errors in establishing the sonoreaction mechanism and/or outcome. The formation of different compounds is closely related to the nature of the gas and frequency used in these experiments. Based on the nature of the compounds identified we advanced a mechanism, involving a dissimilar splitting of unstable radical cation of NB in argon and air respectively. Thus, under air, the formation of phenyl cation is favored and it responsible for the formation of oxygenated light as well as heavy compounds. Under argon, the formation of phenyl radical seems to be favored and the formed phenyl radical reacts faster with phenoxy radical to give diphenylether.

Short sonication time, especially under argon as gas could be considered safe enough for nitrobenzene as solvent. We can conclude that this study offers, besides information of possible artefacts resulting from NB sonication, an unexpected support for electron transfer mechanism between two NB molecules sono-decomposition.

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