

THERMAL DECOMPOSITION OF NITROGUANIDINE

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ABSTRACT

The thermal behaviour of nitroguanidine was studied using differential scanning calorimetry. The decomposition was investigated as a function of heating rate, sample size, inert diluent and type of sample holder, and under an atmosphere of nitrogen or air. An endotherm was observed prior to the exothermic reaction and it is suggested that melting is accompanied by breaking of hydrogen bonds. This interpretation is discussed in relation to the results of the decomposition of nitroguanidine in the accelerating rate calorimeter.

INTRODUCTION

The thermal decomposition of nitroguanidine has been studied for many years but few quantitative data relating to the kinetics have been reported. The decomposition is complex and, although measurements of the products have been reported, interpretation of the mechanism is still tentative. Recently, a kinetic study of the decomposition was reported using the technique of accelerating rate calorimetry (ARC) [1]. The results of this study, together with previous results, clearly showed the difficulty in obtaining values for an activation energy for the decomposition, in comparing values obtained by different techniques, and in interpreting the values in terms of a mechanism or even in terms of thermal stability.

Results from the study using ARC, as well as others, suggested that decomposition may occur simultaneously by more than one pathway and that autocatalysis may be important. Because these effects manifest themselves in different ways in different techniques, more information may be gained by careful comparison of results obtained by different methods. Studies using thermoanalytical techniques generally report one exotherm in the region 220–250 °C [2,3]. Only one study reported an activation energy

for decomposition; Rogers [4], using differential scanning calorimetry (DSC), obtained an activation energy of 21 kcal mol⁻¹. Ripper and Krien [5], using differential thermal analysis (DTA), observed different thermograms for α - and β -nitroguanidine. With α -nitroguanidine, exotherms were observed at 200 and 250°C, while β -nitroguanidine showed a slight, broad endotherm at about 200°C before the main exotherm. In the isothermal studies [6], and in experiments using the flowing afterglow [7] and ARC, decomposition occurred in a lower temperature region, 110–180°C. Measured activation energies in the two regions were very different. Also, significant differences in the products of the reaction were observed with different heating rates [8].

Since nitroguanidine melts at 232°C the mechanism of decomposition in the thermoanalytic techniques may be considerably different from that occurring in the other techniques. To pursue these questions, studies of the decomposition of nitroguanidine were continued using the technique of DSC. The experiments describe the effect of heating rate, sample size, inert diluent, atmosphere and design of sample holder on the kinetic characteristics of the decomposition. An important finding was the occurrence of an endotherm prior to the exotherm. Reasons for this are discussed and related to the results previously obtained using ARC.

EXPERIMENTAL

Materials

Nitroguanidine (NO₂)NH – C(=NH) – NH₂ of minimum purity 99% and average particle diameter 4.3–6.0 μm, was obtained from NiguChemie, Waldkraiburg, F.R.G. The material was stored at room temperature with no further purification. Silica, 240 mesh, used as a diluent, was obtained from Fisher Scientific. Pre-purified nitrogen, 99.998%, and extra-dry air were used to purge the system. Indium was supplied by Du Pont Co.

Apparatus

The equipment used was a Du Pont 9900 thermal analysis system, consisting of a Texas Instrument professional computer with a dedicated Du Pont operating system, CRT display, disk data storage, module interface, plotter and printer. An analysis module, Du Pont 910 differential scanning calorimeter, was controlled by the computer through the module interface. Appropriate software was obtained commercially.

Procedure

The samples were weighed accurately using an electronic microbalance, module Mettler M3, with a reproducibility of $\pm 1 \mu\text{g}$. The sample and reference holders were always positioned accurately in the furnace. Temperature and cell constants were calibrated using an indium standard for each heating rate. Peak area, extrapolated onset temperature, peak maximum and peak height were determined by computer through the General Utility program.

Most decompositions were performed in aluminum crimped pans. For the small sample size, the cover was aligned with the pan and sealed in the sample-encapsulating press. To study the effect of pressure and gaseous products, a variety of sample holders was used. Uniformly sized pinholes were pieced in the lid of the holder to release the pressure. Since the crimp seal on the aluminum pan did not retain a high pressure of gaseous products, a sample holder, hermetically sealed, was used to retain the pressure to 50 psi.

The experiments performed are summarized as follows.

1. Influence of heating rate.
 - Sample size: 1.5 mg
 - Sample holders: aluminum crimped pan
 - Atmosphere: nitrogen, flow rate 50 ml min^{-1}
 - Heating rate: 2.5, 5.0, 10.0, 20.0 and $40.0^\circ \text{C min}^{-1}$
2. Influence of sample size.
 - Sample size: 0.5–1.8 mg
 - Sample holders: aluminum crimped pan
 - Atmosphere: nitrogen, flowrate 50 ml min^{-1}
 - Heating rates: 5.0 and $20.0^\circ \text{C min}^{-1}$
3. Influence of inert diluent.
 - Sample size: (1) nitroguanidine 1.5 mg
 - (2) nitroguanidine 1.5 mg + silica 3.0 mg
 - (3) nitroguanidine 1.5 mg + silica 7.5 mg
 - Sample holders: aluminum crimped pan
 - Atmosphere: nitrogen, flowrate 50 ml min^{-1}
 - Heating rate: 5.0 and $20.0^\circ \text{C min}^{-1}$
4. Influence of sample holders.
 - Sample size: 1 mg
 - Sample holders: (1) hermetically sealed pan
 - (2) aluminum crimped pan
 - (3) aluminum pan with 1 hole in lid
 - (4) aluminum pan with 5 holes in lid
 - (5) aluminum pan without lid
 - Atmosphere: nitrogen, flowrate 50 ml min^{-1}
 - Heating rates: 5.0 and $20.0^\circ \text{C min}^{-1}$

5. Influence of atmosphere.

Sample size: 1 mg

Sample holder: aluminum pan with 5 holes in lid

Atmosphere: nitrogen or air, flowrate 50 ml min⁻¹

Heating rates: 5.0 and 20.0 °C min⁻¹

RESULTS

The first stage of decomposition of nitroguanidine occurred above 230 °C and resulted in a weight loss of between 70 and 80%. At 550 °C a second decomposition was observed, causing a further 20% weight loss, and was probably due to decomposition of the product melanine [6,9]. Only the first stage was investigated further. In the first stage of decomposition an endothermic peak was observed prior to the strong exothermic peak under some conditions. The effect of the five variables on the exothermic peak will be presented first (Section A) and the effects on the endothermic peak second (Section B).

Section A

1. Influence of heating rate

The results of the experiments performed with various heating rates are summarized in Table 1 and a set of thermograms is shown in Fig. 1. The onset temperature of the exothermic reaction was found by extrapolating the

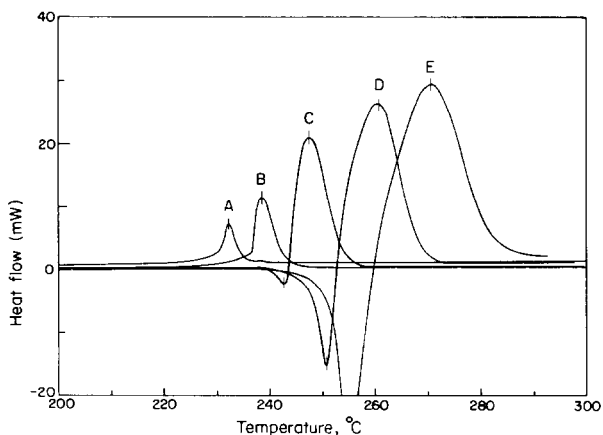


Fig. 1. Influence of the heating rate on the endotherm and the exotherm observed in the thermal decomposition of nitroguanidine. Aluminum crimped pan, nitrogen atmosphere, sample size 1.5 mg. Heating rate: A, 2.5 °C min⁻¹; B, 5 °C min⁻¹; C, 10 °C min⁻¹; D, 20 °C min⁻¹; E, 40 °C min⁻¹.

TABLE 1

Influence of heating rate (aluminum crimped pan; nitrogen atmosphere)

| Heating rate (°C min ⁻¹) | Weight of nitroguanidine (mg) | Onset temperature (°C) | Temperature at peak maximum (°C) | Peak height (mW mg ⁻¹) | Heat of transition (J g ⁻¹) |
|---|-------------------------------------|------------------------------|---|--|---|
| 2.5 | 1.472 | 230 | 232 | 4.37 | 559 |
| 5 | 1.631 | 236 | 238 | 6.96 | 486 |
| 5 | 1.412 | 235 | 237 | 8.74 | 538 |
| 5 | 1.325 | 235 | 237 | 8.75 | 557 |
| 10 | 1.525 | 245 | 248 | 12.7 | 533 |
| 10 | 1.697 | 243 | 247 | 12.0 | 470 |
| 10 | 1.782 | 244 | 248 | 11.7 | 464 |
| 15 | 1.503 | 250 | 255 | 18.1 | 501 |
| 15 | 1.470 | 249 | 255 | 19.2 | 539 |
| 20 | 1.497 | 253 | 261 | 17.3 | 411 |
| 20 | 1.681 | 255 | 263 | 16.4 | 366 |
| 20 | 1.778 | 253 | 261 | 17.2 | 404 |
| 40 | 1.410 | | 271 | | |

leading side of the peak to the intersection with the baseline. Reproducibility within three experiments was $\pm 1^\circ\text{C}$. The onset temperature of decomposition and the peak maximum temperature increased with increasing heating

TABLE 2

Influence of sample size (aluminum crimped pan; nitrogen atmosphere)

| Weight of nitroguanidine (mg) | Onset temperature (°C) | Temperature at peak maximum (°C) | Peak height (mW mg ⁻¹) | Heat of transition (J g ⁻¹) |
|---------------------------------------|------------------------------|--|--|---|
| Heating rate 5.0°C min ⁻¹ | | | | |
| 0.572 | 237 | 238 | 9.8 | 632 |
| 0.592 | 236 | 237 | 10.6 | 669 |
| 1.023 | 236 | 238 | 10.0 | 655 |
| 1.325 | 235 | 237 | 8.8 | 557 |
| 1.412 | 235 | 237 | 8.7 | 538 |
| 1.631 | 237 | 239 | 7.0 | 486 |
| Heating rate 20.0°C min ⁻¹ | | | | |
| 0.504 | | 261 | | |
| 0.549 | 259 | 259 | 17.3 | 429 |
| 0.989 | 255 | 262 | 15.5 | 385 |
| 1.089 | 255 | 262 | 14.3 | 354 |
| 1.497 | 253 | 263 | 17.3 | 411 |
| 1.778 | 253 | 261 | 17.2 | 404 |

rate. In addition, an endotherm, not noticeable at the lowest heating rate, became more pronounced as the heating rate was increased and caused some distortion in the exotherm.

2. Influence of sample size

The results of experiments using samples weighing between 0.5 and 1.8 mg are summarized in Table 2. With heating rates of $5^{\circ}\text{C min}^{-1}$ and $20^{\circ}\text{C min}^{-1}$, the extrapolated onset temperatures were 235°C and 245°C respectively. Peak height was expressed per unit mass and was reasonably constant for a particular heating rate in this range of sample size. It should be noted that the calculation of the heat of transition may be sensitive to the baseline conditions.

3. Influence of diluent

Silica was mixed with nitroguanidine in the ratios of 1:2 and 1:5, keeping the quantity of nitroguanidine at 1.5 mg for all the experiments. Experiments were performed with heating rates of $5^{\circ}\text{C min}^{-1}$ and $20^{\circ}\text{C min}^{-1}$, and the results are given in Table 3. With both heating rates, dilution

TABLE 3

Influence of inert diluent (aluminum crimped pan; nitrogen atmosphere)

| Weight of nitroguanidine (mg) | Total weight of sample (mg) | Onset temperature ($^{\circ}\text{C}$) | Temperature at peak maximum ($^{\circ}\text{C}$) | Peak height (mW mg^{-1}) | Heat of transition (J g^{-1}) |
|---|-----------------------------|--|--|-------------------------------------|--|
| Heating rate $5.0^{\circ}\text{C min}^{-1}$ | | | | | |
| 1.631 | 1.631 | 237 | 239 | 6.96 | 486 |
| 1.412 | 1.412 | 235 | 237 | 8.74 | 538 |
| 1.325 | 1.325 | 235 | 237 | 8.75 | 557 |
| 1.577 | 4.730 | 237 | 240 | 7.92 | 611 |
| 1.428 | 4.285 | 238 | 241 | 8.44 | 629 |
| 1.448 | 4.345 | 238 | 241 | 7.25 | 554 |
| 1.406 | 8.438 | 235 | 239 | 6.30 | 553 |
| 1.475 | 8.849 | 237 | 240 | 6.88 | 576 |
| 1.394 | 8.362 | 236 | 240 | 6.53 | 560 |
| Heating rate $20^{\circ}\text{C min}^{-1}$ | | | | | |
| 1.497 | 1.497 | 253 | 261 | 17.3 | 412 |
| 1.681 | 1.681 | 255 | 263 | 16.4 | 366 |
| 1.778 | 1.778 | 253 | 261 | 17.2 | 404 |
| 1.488 | 4.463 | 254 | 262 | 25.7 | 591 |
| 1.337 | 4.010 | 254 | 262 | 25.2 | 602 |
| 1.328 | 3.983 | 255 | 262 | 22.8 | 561 |
| 1.468 | 8.806 | 254 | 262 | 24.3 | 633 |
| 1.449 | 8.692 | 254 | 262 | 23.0 | 580 |
| 1.570 | 9.418 | 254 | 262 | 23.6 | 612 |

with silica did not affect the temperature of onset of decomposition nor the temperature at the peak maximum. The peak height and heat of reaction were again normalized to the amount of nitroguanidine. At a heating rate of $20^{\circ}\text{C min}^{-1}$ the diluted samples appeared to have a higher peak height and heat of reaction.

4. Influence of sample holders

Table 4 presents the results of decomposition with the various sample holders at heating rates of $5^{\circ}\text{C min}^{-1}$ and $20^{\circ}\text{C min}^{-1}$ and Fig. 2 shows some of the thermograms at a heating rate of $20^{\circ}\text{C min}^{-1}$. Decomposition in the sealed pan occurred at the lowest temperature and gave the highest peak height. The weight loss was about 72% compared with 80% in the open pan. With a heating rate of $5^{\circ}\text{C min}^{-1}$ the extrapolated onset temperature was about 15°C lower than in the open pan. These results show that the products of the decomposition cause a marked acceleration in the rate of decomposition.

TABLE 4
Influence of sample holder (nitrogen atmosphere)

| Sample holder (see experi- mental) | Weight of nitro- guanidine (mg) | Weight loss (%) | Onset temper- ature ($^{\circ}\text{C}$) | Temperature at peak maximum ($^{\circ}\text{C}$) | Peak height (mW mg^{-1}) | Heat of transition (J g^{-1}) |
|--|--|-----------------------|---|---|---|--|
| Heating rate $5^{\circ}\text{C min}^{-1}$ | | | | | | |
| 1 | 1.071 | 68.7 | 229 | 232 | 16.2 | 645 |
| 1 | 1.053 | 68.8 | 231 | 233 | 14.4 | 645 |
| 2 | 1.412 | | 235 | 237 | 8.7 | 538 |
| 2 | 1.325 | | 235 | 237 | 8.7 | 557 |
| 3 | 1.110 | 78.8 | 240 | 242 | 9.6 | 583 |
| 3 | 1.059 | 77.1 | 240 | 243 | 9.5 | 574 |
| 4 | 0.942 | | 243 | 244 | 7.7 | 495 |
| 4 | 0.967 | 72.3 | 242 | 244 | 7.9 | 547 |
| 5 | 0.914 | 80.1 | 246 | 248 | 5.5 | 296 |
| 5 | 1.189 | 78.4 | 245 | 248 | 6.1 | 336 |
| Heating rate $20^{\circ}\text{C min}^{-1}$ | | | | | | |
| 1 | 0.999 | 72.4 | 252 | 257 | 40.9 | 703 |
| 1 | 1.033 | 72.3 | 252 | 257 | 45.6 | 735 |
| 2 | 0.989 | 75.7 | 255 | 262 | 15.5 | 385 |
| 2 | 1.089 | 77.0 | 255 | 262 | 14.3 | 354 |
| 3 | 0.949 | 77.0 | 258 | 265 | 16.1 | 368 |
| 3 | 1.099 | 78.2 | 257 | 264 | 16.0 | 351 |
| 4 | 0.933 | 78.8 | 255 | 264 | 19.2 | 402 |
| 4 | 1.127 | 77.2 | 255 | 263 | 23.0 | 468 |
| 5 | 1.089 | | 258 | 266 | 21.3 | 349 |
| 5 | 0.988 | 80.1 | 257 | 266 | 19.4 | 322 |

TABLE 5

Influence of atmosphere (aluminum crimped pan with 5 holes)

| Atmosphere | Weight of nitroguanidine (mg) | Weight loss (%) | Onset temperature ($^{\circ}\text{C}$) | Temperature at peak maximum ($^{\circ}\text{C}$) | Peak height (mW mg^{-1}) | Heat of transition (J g^{-1}) |
|--|-------------------------------|-----------------|--|--|-------------------------------------|--|
| Heating rate $5^{\circ}\text{C min}^{-1}$ | | | | | | |
| N_2 | 0.942 | | 243 | 245 | 7.71 | 495 |
| N_2 | 0.967 | 72.3 | 242 | 244 | 7.92 | 547 |
| Air | 0.901 | 77.4 | 244 | 247 | 5.93 | 370 |
| Air | 1.133 | 72.3 | 243 | 245 | 7.56 | 446 |
| Heating rate $20^{\circ}\text{C min}^{-1}$ | | | | | | |
| N_2 | 1.127 | 77.2 | 255 | 263 | 23.0 | 468 |
| N_2 | 0.933 | 78.8 | 255 | 264 | 19.2 | 402 |
| Air | 1.011 | 79.6 | 255 | 263 | 18.9 | 401 |
| Air | 0.954 | 77.9 | 256 | 264 | 19.5 | 412 |

5. Influence of atmosphere

Using the aluminum pan with five pinholes in the lid the decomposition was measured at a heating rate of $20^{\circ}\text{C min}^{-1}$ under a nitrogen and an air atmosphere. The onset temperature and maximum temperature were essentially the same under both atmospheres. Results are given in Table 5.

TABLE 6

Characteristics of the endothermic peak

| Weight of nitroguanidine (mg) | Weight of silica (mg) | Heating rate ($^{\circ}\text{C min}^{-1}$) | Onset temperature ($^{\circ}\text{C}$) | Temperature at peak maximum ($^{\circ}\text{C}$) | Heat of transition (J g^{-1}) |
|-------------------------------|-----------------------|--|--|--|--|
| Aluminum crimped pan | | | | | |
| 1.7 ^a | 0 | 10 | 240 | 242 | 20 |
| 1.5 ^a | 3.0 | 10 | 241 | 244 | 21 |
| 1.6 ^a | 0 | 20 | 248 | 251 | 96 |
| 1.4 ^a | 2.7 | 20 | 250 | 252 | 104 |
| 1.5 ^a | 7.5 | 20 | 247 | 251 | 95 |
| 1.4 | 0 | 40 | | 255 | |
| 1.4 | 2.9 | 40 | | 256 | |
| 1.5 | 7.6 | 40 | | 255 | |
| Hermetically sealed pan | | | | | |
| 1.0 ^a | 0 | 20 | 249 | 251 | 73 |
| Open pan | | | | | |
| 1.0 ^a | 0 | 5 | 243 | 245 | 30 |
| 1.1 ^a | 0 | 20 | 252 | 255 | 172 |

^a Average of 2 or 3 experiments.

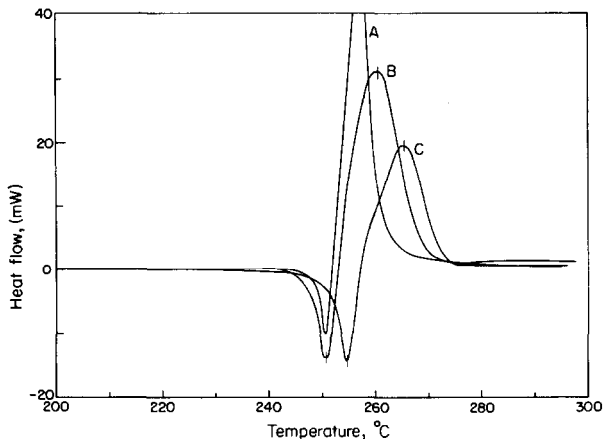


Fig. 2. Influence of the sample holders on the thermal decomposition of nitroguanidine. Nitrogen atmosphere, heating rate $20^{\circ}\text{C min}^{-1}$, sample size 1 mg. Sample holders: A, hermetically sealed pan; B, aluminum crimped pan; C, aluminum pan without lid.

Section B

The effect of the variables on the characteristics of the endotherm are summarized in Table 6. An increase in heating rate increased the onset temperature of the endotherm and the temperature at the minimum of the peak. The shift was comparable with but less than the shift observed for the exothermic peak (Table 1). The sealed pans showed similar temperatures at the minimum but in the open pan a higher temperature at the minimum was observed (Fig. 2). Mixing with an inert diluent had negligible effect.

DISCUSSION

The most striking feature of the thermograms is the endotherm which occurs just prior to the exothermic reaction. Such endotherms are usually attributed to melting, but the endothermic peaks observed in these experiments show features unlike those usually observed with melting. The peaks are broad and the onset temperatures shift considerably with the heating rate and with the degree of confinement of the product gases. This behavior is not occasioned by the apparatus. The melting points of several solids (trinitrotoluene, Tetryl, ammonium nitrate and indium metal) were measured using heating rates of $10^{\circ}\text{C min}^{-1}$ and $20^{\circ}\text{C min}^{-1}$. The peaks were sharp and the onset temperatures of the endotherms for these two heating rates differed by only about 1°C . By contrast, the onset temperatures of the endotherms observed with nitroguanidine differed by about 7°C for these two heating rates (Table 6).

It is likely that melting of nitroguanidine is the primary cause of the endotherm. The melting point of nitroguanidine is 232°C, although higher melting points have been reported. The onset temperature of the endotherm varied from 240 to 252°C, depending on the experimental conditions, and some indication of a lower melting point was evident in the thermograms with heating rates of 2.5 and 5°C min⁻¹. An asymmetry in these curves suggests an endothermic effect just prior to the exothermic reaction. Nevertheless, the shape of the peaks and the range of temperature covered by the minima suggest that the process is not a simple melting of the solid and that some chemical changes are taking place at the same time.

Solid nitroguanidine has strong inter- and intra-molecular hydrogen bonds [9]. It has been suggested that the intra-molecular hydrogen bonds, in particular, are important in contributing to the weakening of certain bonds in the molecule and hence in determining the pathway for decomposition. Breaking of these bonds may precede decomposition under some conditions and would be observed as an endothermic process. This interpretation is consistent with the results of a previous study of the decomposition of nitroguanidine using the accelerating rate calorimeter [1]. These results indicated that the decomposition involved at least two distinct stages. In the early stages of the decomposition a process occurred with a very low activation energy of the order of 20 kcal mol⁻¹. At later stages, as the decomposition progressed, the large exothermicity of the reaction caused a very rapid increase in rate and an apparently high activation energy for decomposition. Thus the process observed as occurring with a low activation energy in the accelerating rate calorimeter in the initial stages of the decomposition may be related to the process which appears as an endothermic reaction in the differential scanning calorimeter. The breaking of hydrogen bonds is a weakly endothermic process which could lead to rearrangements preceding the rapid exothermic decomposition of the molecule.

The results of the present study are also consistent with the earlier results regarding the effect of accumulation of reaction products on the rate of decomposition. In the previous study in the accelerating rate calorimeter confinement of the products in the bomb gave a faster rate of decomposition at a lower temperature. The same effect was observed in the present study, as illustrated in Fig. 2. In both systems, the reaction products have a strong accelerating effect on the rate of decomposition.

The shifting of the endothermic peaks with increasing heating rate probably distorts the exothermic peak and makes the estimation of the activation energy unreliable. The overlapping endothermic peak would have the effect of reducing the maximum temperature of the exothermic peak for a particular heating rate. This in turn would reduce the estimated value of the activation energy. Using the method ASTM E698 described by the manufacturer an activation energy of 32 kcal mol⁻¹ was derived, which may

therefore be regarded as a lower limit. The various activation energies reported for the decomposition of nitroguanidine were discussed in the previous study [1].

SUMMARY

The endotherm observed in the initial stages of the decomposition of nitroguanidine in the differential scanning calorimeter has been suggested to involve melting accompanied by breaking of hydrogen bonds. The results indicate two distinct stages in the decomposition process, in agreement with the interpretation of the results of the decomposition in the accelerating rate calorimeter.

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