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THE PYROLYSIS OF TRIMETHYLGERMANE AND TRIMETHYLSILANE

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Summary

The number of products and the H_2/CH_4 ratio obtained from the flow pyrolyses of $(CH_3)_3GeH$ and $(CH_3)_3SiH$ were very different. The $(CH_3)_3GeH$ decomposition is consistent with the following mechanism:

$(CH_3)_3GeH \rightarrow (CH_3)_3Ge^{\cdot} + H^{\cdot}$
$(CH_3)_3GeH \rightarrow (CH_3)_2\dot{G}eH + {}^{\cdot}CH_3$
${}^{\cdot}CH_3(H^{\cdot}) + (CH_3)_3GeH \rightarrow (CH_3)_3Ge^{\cdot} + CH_4(H_2)$
$(CH_3)_3Ge^{\cdot} \rightarrow (CH_3)_2Ge + {}^{\cdot}CH_3$
$(CH_3)_2Ge + (CH_3)_3GeH \rightarrow (CH_3)_5Ge_2H$
$2(CH_3)_3Ge^{\cdot} \rightarrow (CH_3)_6Ge_2$

The pyrolysis of $(CH_3)_3SiH$ was found to be much more complex, presumably due to the formation of silicon—carbon double bonded intermediates and the $(CH_3)_2Si(H)CH_2^{\cdot}$ radical. We also present data which supports the presence of a H atom chain sequence during this pyrolysis.

Introduction

Double bonded (or biradical) silicon—carbon intermediates have been proposed as precursors to the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane [1, 2] and other 1,3-disilacyclobutanes [2]. These intermediates appear to be present during the pyrolysis of $(CH_3)_3SiH$ [2]. We have studied the pyrolysis of $(CH_3)_3GeH$ in an effort to elucidate the decomposition mechanism and to examine the possibility of the formation of "double bonded" germanium—carbon intermediates. We have also examined the pyrolysis of $(CH_3)_3SiH$ under similar conditions to compare the decompositions of these analogous compounds.

Experimental

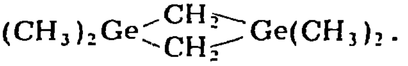
Trimethylgermane and $(CH_3)_3SiH$ were prepared by the $LiAlH_4$ reduction of their respective chlorides. They were identified by their infrared and mass spectra and their purity was checked by GLPC.

The $(CH_3)_3GeH$ pyrolyses were carried out in a flow system containing an automatic Toepler pump, a thermal zone and a "U" trap. The 15 cm thermal zone was constructed of 1 cm OD Vycor tubing and heated by a heating tape. A thermometer was seated in a pyrex well between the heating tape and the Vycor tubing. The heating assembly was well insulated with layers of asbestos tape. A germanium mirror was deposited in the thermal zone by the pyrolysis of GeH_4.

Pyrolysis of trimethylgermane

In a typical experiment, $(CH_3)_3GeH$ (1.1 mmol) was pyrolyzed for 6 h at 470° with the "U" trap cooled to —63°. The product fraction which passed a —196° trap (0.19 mmol) was Toepler pumped into a calibrated volume for quantitative determination. A mass spectrum of this fraction demonstrated that it was CH_4 and H_2 in about a 30/1 ratio. The fraction condensed at —196° was separated by trap to trap distillation. The fraction condensed at —196° having passed a —63° trap (0.80 mmol) was $(CH_3)_3GeH$. This fraction was identified by an infrared and mass spectra and by GLPC. The fraction condensed at —78° (0.059 mmol), was identified as a mixture of $(CH_3)_5Ge_2H$ and $(CH_3)_6Ge_2$. The GLPC chromatogram of this mixture consisted of only two peaks. The retention time of the smaller peak corresponded to that of an authentic sample of $(CH_3)_6Ge_2$.

The infrared spectrum of this mixture was essentially identical to that reported for $(CH_3)_5Ge_2H$ [3]. The proton NMR spectrum in $DCCl_3$ (for δ between 1 and 0) consisted of two resonances at δ 0.267 and 0.325 (rel. int. 4.2/1) and a resonance at 0.21 ppm The resonances at δ 0.267 and 0.325 are from $(CH_3)_3GeGe(CH_3)_2H$ [3] consisting of a singlet at 0.267 ($3CH_3$) and a doublet centered at 0.297 ppm ($2CH_3$) with J 4 Hz. Thus the relative intensities at δ 0.267 and 0.325 ppm should be 4/1. The resonance at δ 0.21 ppm is due to $(CH_3)_6Ge_2$ [4]. The ratio $(CH_3)_5Ge_2H/(CH_3)_6Ge_2$ was determined to be 4.15 from this NMR spectrum.

The mass spectrum (70 eV) of this mixture confirmed the presence of $(CH_3)_6Ge_2$ and $(CH_3)_5Ge_2H$ and the absence of the germacyclobutane,  $(CH_3)_2Ge(CH_2)_2Ge(CH_3)_2$. The peak intensities between *m/e* 230—240 were identical to those of an authentic sample of $(CH_3)_6Ge_2$. These relative intensities compared to those of $(CH_3)_6Ge_2$ were 1.00, 1.00, 1.03 and 0.96 at *m/e* 238, 236, 234 and 232 which are the most intense peaks of $(CH_3)_6Ge_2$ in the *m/e* region 230—240. The peaks in this region are all from the $(CH_3)_6Ge_2^+$ ion with different germanium isotopes. The presence of $(CH_3)_2Ge(CH_2)_2Ge(CH_3)_2$, with a molecular weight two units lower than $(CH_3)_6Ge_2$, would change these ratios significantly. The mass peaks between *m/e* 215—226 demonstrated the presence of $(CH_3)_5Ge_2H$.

Pyrolysis of trimethylgermane in the presence of 1,3-C_4H_6. The pyrolysis of $(CH_3)_3GeH$ and 1,3-C_4H_6 (0.3 mmol each) was carried out at 500° for 3 h with the cold trap set at −63°. The vapor phase ratio was calculated to be 1/4. The product fraction which passed a −196° trap was CH_4 and H_2 (0.45 mmol). The fraction condensed at −196° which passed a −78° trap was $(CH_3)_3GeH$ and 1,3-C_4H_6 (0.36 mmol). The fraction condensed at −78° (0.07 mmol) did not contain $(CH_3)_6Ge_2$ or $(CH_3)_5Ge_2H$. The mass spectrum of this fraction had peaks in the region *m/e* 176—170 with the highest intense peak at *m/e* 174. These peaks would be consistent with $(CH_3)_3GeCH_2C(H)=C(H)CH_3$ with a molecular weight of 174 with ^{74}Ge (most abundant isotope at 37%). Peaks in the *m/e* region 160—154 were also present with the highest major peak at *m/e* 158. This would be consistent for 1,1-dimethylgermacyclopent-3-ene with a molecular weight of 158 with ^{74}Ge. The mass spectrum would suggest that the germacyclopent-3-ene was present in largest quantity.

Pyrolysis of trimethylsilane

The pyrolyses of $(CH_3)_3SiH$ were carried out in a quartz tube. The thermal zone, 3.5 × 1.6 cm (diameter), was surrounded by a Lindberg heating unit (Model 50431) which was set in brick and insulated by asbestos block. The quartz interior was coated with a silicon mirror deposited by the thermolysis of SiH_4. A high temperature thermometer was set between the quartz tube and the heating unit. The quartz tube was preceded by an automatic Toepler pump and followed by two "U" traps.

In a typical experimental sequence $(CH_3)_3SiH$ (0.41 mmol) was condensed into one "U" trap at −196°. A low temperature slush bath (−83°, −78°, −63° or −57°) was placed on the other "U" trap. The pressures of $(CH_3)_3SiH$ in the flow system were 27.5, 20.5, 7.0 and 3.5 mm when the −57, −63, −78 and −83° slush baths were used. The oven temperature (~ 710°) was recorded and the Toepler pump was set into operation. The liquid nitrogen bath (−196°) was removed and the $(CH_3)_3SiH$ vaporized. After 15 minutes, the −196° bath was replaced and the Toepler pump allowed to operate for 5 minutes. A Teflon valve between the oven and Toepler pump was closed. The Toepler pump was now operated to compress the H_2—CH_4 product mixture into a small calibrated volume for quantitative determination. A sample of this mixture was then analyzed mass spectroscopically to determine the H_2/CH_4 ratio. The mass spectrometer was calibrated with known mixtures of H_2 and CH_4. The H_2—CH_4 mixture was pumped off and the experiment was repeated with the same sample of $(CH_3)_3SiH$. However, the surface now was at least partially coated with a polymeric product from the last pyrolysis.

The initial H_2—CH_4 fractions produced over a fresh surface* from pyrolyses carried out with a −57, −63, −78 and −83° cold trap had H_2/CH_4 ratios of 1.17 ± 0.1, 1.25 ± 0.1, 2.11 ± 0.2 and 3.25 ± 0.3 respectively. The successive pyrolyses over polymerically coated surfaces produced H_2/CH_4 ratios that were higher than those of the initial runs. As an example, for pyrolyses with a −63° cold trap, the H_2/CH_4 ratio was 1.25, 1.59, 1.51, 1.67, 1.89, 1.85 and 2.18 for successive 15 minute pyrolyses with the same $(CH_3)_3SiH$ over a surface

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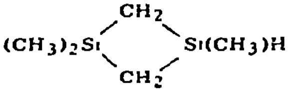
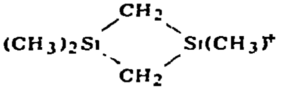
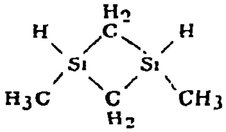
* The same results were obtained over a silicon mirror and a silicon—carbon surface which resulted from the 24 h heating, in situ, of the polymeric product at the reaction temperature (710°).

TABLE 1

MASS SPECTRUM OF HEAVY PRODUCTS FROM PYROLYSIS OF $(CH_3)_3SiH$ (15 eV)

m/e	Relative intensity	Suggested products
146	0.13	$(CH_3)_6Si_2$ $(CH_3)_3SiCH_2Si(CH_3)_2H$ $(CH_3)_2Si(H)C_2H_4Si(CH_3)_2H$
144	0.05	$[(CH_3)_2SiCH_2]_2$
132	0.22	$(CH_3)_5Si_2H$
131	0.55	$(CH_3)_5Si_2^+$
130	0 80	
129	0.12	
118	0.17	$(CH_3)_4Si_2H_2$
117	0.86	$(CH_3)_4Si_2H^+$
116	0.79	P[a]
115	0.85	P-1
101	0 45	P-15
73	1 00	$(CH_3)_3Si^+$

[a] P is



covered each time by more polymeric product. For the experiments with the −83° cold bath, this ratio went as high as 4.60 on a seventh pyrolysis.

In a few experiments the product fraction condensed in the cooled "U" trap was analyzed gas chromatographically and mass spectroscopically. The gas chromatogram contained nine major and three very minor peaks for compounds heavier than $(CH_3)_4Si$. In Table 1, we list a typical mass spectrum of the heavy product fraction at 15 eV where peaks are primarily due to parent ions.

The pyrolysis was also carried out in the same reaction tube after quartz rods were dropped into the thermal zone. These rods were coated with a silicon mirror from SiH_4 pyrolyses. The quartz rods increased the surface to volume ratio by 6.84. The H_2/CH_4 ratio (with a −57° bath) was approximately 1.14 both before and after the beads were added. In 15 minute pyrolyses, the quantity of the H_2—CH_4 mixture produced was 0.43 and 0.38 mmol in the unpacked vessel and 0.23 and 0.21 mmol in the packed vessel. The reaction volume of the packed reaction tube was 33% less than that of the unpacked reaction tube. The quantity of the H_2—CH_4 mixture normally decreased from run to run as more polymer was deposited.

Results

Trimethylgermane

The volatile products from the pyrolysis of $(CH_3)_3GeH$ in a flow system at 470°, with a −63° trap present to remove less volatile products, were CH_4 and H_2 in a 30/1 ratio and $(CH_3)_5Ge_2H$ and $(CH_3)_6Ge_2$ in a 4/1 ratio. The absence of even small quantities of germacyclobutanes was also demonstrated by mass spectra, GLPC and proton NMR spectroscopy. This pyrolysis was also carried out in the presence of a 4/1 excess of 1,3-C_4H_6. In this experiment, the formation of $(CH_3)_5Ge_2H$ and $(CH_3)_6Ge_2$ ceased while $GeH_3CH_2C(H){=}CHCH_3$ and 1,1-dimethylgermacyclopent-3-ene were the probable products along with vinylcyclohexene, a product from the neat pyrolysis of 1,3-C_4H_6.

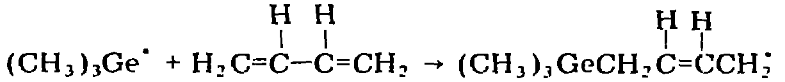
The above results are consistent with the following mechanism:

$$(CH_3)_3GeH \rightarrow (CH_3)_3Ge^{\bullet} + H^{\bullet} \qquad (1)$$
$$(CH_3)_3GeH \rightarrow (CH_3)_2\dot{G}eH + {}^{\bullet}CH_3 \qquad (2)$$
$${}^{\bullet}CH_3(H^{\bullet}) + (CH_3)_3GeH \rightarrow (CH_3)_3Ge^{\bullet} + CH_4(H_2) \qquad (3)$$
$$(CH_3)_3Ge^{\bullet} \rightarrow (CH_3)_2Ge + {}^{\bullet}CH_3 \qquad (4)$$
$$(CH_3)_2Ge + (CH_3)_3GeH \rightarrow (CH_3)_5Ge_2H \qquad (5)$$
$$2(CH_3)_3Ge^{\bullet} \rightarrow (CH_3)_6Ge_2 \qquad (6)$$

A decomposition similar to that proposed for reaction 4 occurs in the pyrolysis of $(CH_3)_3Ga$. The first step is loss of a CH_3 radical from $(CH_3)_3Ga$, while the second is the loss of a second CH_3 radical from the $(CH_3)_2Ga^{\bullet}$ radical (eqn. 7) [5].

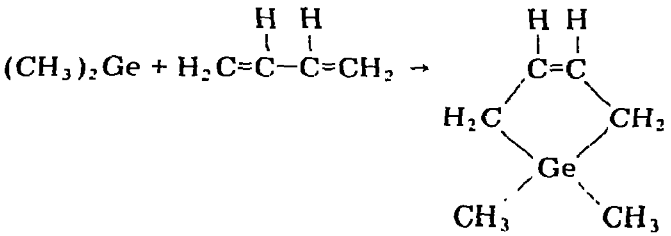
$$(CH_3)_2Ga^{\bullet} \rightarrow (CH_3)Ga + {}^{\bullet}CH_3 \qquad (7)$$

The results with 1,3-C_4H_6 present are consistent with the presence of both $(CH_3)_3Ge^{\bullet}$ radical and $(CH_3)_2Ge$ [eqns. 8—10].



$$(CH_3)_3Ge^{\bullet} + H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2 \rightarrow (CH_3)_3GeCH_2\overset{H}{C}{=}\overset{H}{C}CH_2^{\bullet} \qquad (8)$$

$$(CH_3)_3GeCH_2\overset{H}{C}{=}\overset{H}{C}CH_2^{\bullet} \xrightarrow[\text{H-abstraction}]{} (CH_3)_3GeCH_2\overset{H}{C}{=}\overset{H}{C}CH_3 \qquad (9)$$



(10)

Trimethylsilane

The pyrolysis of $(CH_3)_3SiH$ was examined at 710° in a flow system containing a cold "U" trap that removed products less volatile than $(CH_3)_3SiH$. The pyrolyses were carried out over a silicon mirror or a silicon—carbon surface obtained from the pyrolysis of the polymer formed in these reactions. Both surfaces produced the same results. The products included H_2 and CH_4. The H_2/CH_4 product ratio increased as the pressure of $(CH_3)_3SiH$ decreased. The ratio was 1.17 ± 0.1, 1.25 ± 0.1, 2.11 ± 0.2 and 3.25 ± 0.3 at $(CH_3)_3SiH$ pressures of 27.5, 20.5, 7.0 and 3.5 mm respectively. The above results were obtained over a fresh silicon or silicon—carbon surface. The H_2/CH_4 ratios obtained in pyrolyses over surfaces containing polymeric product increased essentially as a function of total reaction over that surface. Thus any error in the above ratios due to secondary reactions due to polymeric product decomposition would have increased most for the pyrolyses at highest pressure. We can thus conclude that the H_2/CH_4 ratio increase with a decrease in the $(CH_3)_3SiH$ pressure was not due to secondary effects.

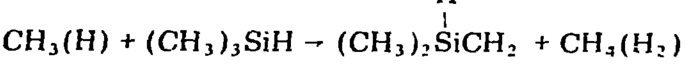
A gas chromatogram of the heavy product fraction demonstrated the presence of 9 major products and possibly 3 minor products. The mass spectrum of this mixture is listed in Table 1. This mass spectrum can be accounted for by the compounds listed in Table 1. These are the same compounds suggested as products by Davidson and Lambert [2] who identified them solely by a mass spectrum

The $(CH_3)_3SiH$ pyrolysis over a silicon mirror was examined as a function of surface to volume ratio. This ratio was increased by 6.84 while the H_2/CH_4 ratio remained constant. The total H_2—CH_4 product fraction decreased in quantity by about 45%. This lower rate was due to a 33% decrease in reaction volume (same pressure) and about a 12% decrease caused by a lower temperature in the thermal zone. The lower temperature was the result of polymer deposition inside the thermal zone acting as an insulating layer. These data strongly suggest that the $(CH_3)_3SiH$ pyrolysis is homogeneous over a silicon mirror and the silicon—carbon polymer deposited during the reaction.

Discussion

The gas phase pyrolysis of $(CH_3)_3GeH$ was found to produce only four volatile products whose formation could be explained by eqns. 1—6. This result was very different from that of the gas phase stirred-flow pyrolysis of $(CH_3)_3$-SiH reported by Davidson and Lambert where eleven products including disilacyclobutanes were obtained [2]. Since our investigation of the pyrolysis of $(CH_3)_3GeH$ was carried out under somewhat different conditions than that of Davidson and Lambert, we repeated the pyrolysis of $(CH_3)_3SiH$ under the same conditions we had used for the pyrolysis of $(CH_3)_3GeH$. In our $(CH_3)_3SiH$ pyrolysis. we obtained the same array of products reported by Davidson and Lambert [2]. Thus the pyrolyses of $(CH_3)_3SiH$ and $(CH_3)_3GeH$ are indeed very different.

The additional products in the $(CH_3)_3SiH$ pyrolysis can be accounted for by the presence of silicon—carbon double bonded intermediates such as $(CH_3)_2Si{=}CH_2$ and $H_3CSi(H){=}CH_2$ and the presence of the $(CH_3)_2Si(H)CH_2^{\cdot}$ radical [2]. Reactions represented by eqns. 1—3 for $(CH_3)_3GeH$ are presumed common to both systems. For $(CH_3)_3SiH$, reaction 11, can apparently compete



$$CH_3(H) + (CH_3)_3SiH \rightarrow (CH_3)_2\overset{\overset{H}{|}}{Si}CH_2^{\cdot} + CH_4(H_2) \qquad (11)$$

with the silicon analog of reaction 3. For $(CH_3)_3GeH$, abstraction of a proton from the methyl group cannot occur in competition with abstraction of the germyl proton. This is the result of the following relative bond energies: carbon—hydrogen > silicon—hydrogen > germanium—hydrogen [6, 7]. Thus in $(CH_3)_3SiH$, H atom abstraction by a methyl radical (or H atom) can take place at carbon (favored numerically) and silicon (favored by lower activation energy) [7] while in $(CH_3)_3GeH$, the abstraction only occurs at germanium due to a presumed much lower activation energy.

The double-bonded intermediates $(CH_3)_2Si{=}CH_2$ and $H_3CSi(H){=}CH_2$ are presumed to arise from the $(CH_3)_2Si(H)CH_2^{\bullet}$ radical. Davidson and Lambert suggested that chain sequences were absent and thus the double-bonded intermediates could not arise from a unimolecular decomposition of the $(CH_3)_2Si(H)CH_2^{\bullet}$ radical. They suggested that this radical underwent disproportionation reactions such as represented by eqn. 12.

$$(CH_3)_2Si(H)CH_2^{\bullet} + (CH_3)_3Si^{\bullet} \rightarrow (CH_3)_3SiH + (CH_3)_2Si{=}CH_2 \qquad (12)$$

It has now been established by Walsh and Wells [8], by this study, and apparently also by Davidson and Howard [8], that the $(CH_3)_3SiH$ decomposition does contain chain processes, at least for H_2 formation. Thus it is possible that the double-bonded intermediates are formed by unimolecular decompositions of the $(CH_3)_2Si(H)CH_2^{\bullet}$ radical, as shown by eqns. 13 and 14.

$$(CH_3)_2Si(H)CH_2^{\bullet} \rightarrow (CH_3)_2Si{=}CH_2 + H^{\bullet} \qquad (13)$$

$$(CH_3)_2Si(H)CH_2^{\bullet} \rightarrow CH_3SiH{=}CH_2 + CH_3^{\bullet} \qquad (14)$$

The results obtained by Walsh and Wells demonstrated that in the pyrolysis of $(CH_3)_3SiH$, short chains occur in the formation of H_2 [8]. We found that the ratio of H_2/CH_4 produced increased as the pressure decreased. This would be consistent with the presence of chain sequences. The formation of $(CH_3)_2Si{=}CH_2$ by reaction 13 could be the chain propagation step for H_2 formation since the H atoms formed would react by the silicon analog of reaction 3 or by reaction 11 If $CH_3SiH{=}CH_2$ is formed by reaction 14, a chain process would be operative for CH_4 formation since the $^{\bullet}CH_3$ radicals would react in the same manner as H atoms. Since the chain propagation steps proposed involve unimolecular decompositions of the same species $[(CH_3)_2Si(H)CH_2^{\bullet}]$, the change in H_2/CH_4 product ratio could be explained by one or both unimolecular decomposition routes taking place in their fall-off region. Calculations using reasonable estimates of parameters suggest that the experimental pressures were too high for either route to be in its low pressure fall-off region. Thus it would appear that the H atom chain sequence exists while the $^{\bullet}CH_3$ radical chain sequence does not*. This conclusion is consistent with the experimental *A* factors determined for the pyrolysis of $(CH_3)_3SiH$ by Davidson and Lambert [2]. They obtained *A* factors of $10^{15.9}$ and $10^{15.6}$ for CH_4 and H_2 formation respectively. Estimated values for non-chain mechanisms would be $10^{16.2}$ and $10^{14.5}$ respectively**. The high experimental value obtained for H_2 formation is strongly suggestive of a H atom chain mechanism while the experimental value obtained for CH_4 formation is essentially that expected for the silicon analog of reaction 2.

The increase in the H_2/CH_4 ratio as the pressure of $(CH_3)_3SiH$ decreased can be accounted for by an increase in the H atom chain length with decreasing $(CH_3)_3SiH$ pressure***.

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* This implies that $D[^{\bullet}CH_2(H)Si(CH_3){-}CH_3] > D[^{\bullet}CH_2(CH_3)_2Si{-}H]$.

** For the process, $(CH_3)_3SiH \rightarrow (CH_3)_3Si + H$, the value of $10^{14.5}$ was calculated from transition state theory and is a maximum value based on lowering of two H atom bending vibrations in the transition state. For hydrocarbons these processes have *A* factors of about 10^{14}. For the process, $(CH_3)_3SiH \rightarrow (CH_3)_2Si(H)^{\bullet} + {}^{\bullet}CH_3$, the *A* factor should be greatly increased due to lower frequencies for motions involving the leaving methyl groups. For hydrocarbons these values [9, 10] range between 10^{16}–10^{17} and the best value [10] for isobutane is $10^{16.2}$.

*** The steps involved in H_2 formation are the silicon analog of reactions 1,3 (with H), 11 (with H) and 13 followed by dimerization of double bonded intermediates and recombination of silyl radicals For a chain to exist it is required that $k_{11} > k_3$ and that reaction 13 be faster than recombination reactions involving the $(CH_3)_2Si(H)CH_2^{\bullet}$ radical. With these assumptions, the chain length of the H atom chain sequence is proportional to the pressure of $(CH_3)_3SiH^{-1/2}$.

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