Kinetics of the Thermal Isomerization of 1,1,2-Trimethylcyclopropane

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> ABSTRACT: The Arrhenius parameters for the gas phase, unimolecular structural isomerizations of 1,1,2-trimethylcyclopropane to three isomeric methylpentenes and two dimethylbutenes have been determined over a wide range of temperatures, 688-1124 K, using both static and shock tube reactors. For the overall loss of reactant, $E_a = 63.7 (\pm 0.5)$ kcal/mol and $\log_{10} A = 15.28 (\pm 0.12)$. These values are higher by 2.6 kcal/mol and 0.7–0.8 than previously reported from experimental work or predicted from thermochemical calculations. E_a for the formation of trans-4-methyl-2-pentene is 1.5 kcal/mol higher than Ea for the formation of the cis isomer, which is identical to the E_a difference previously reported for the formation of trans- and cis-2-butene from methylcyclopropane. Substitution of methyl groups for hydrogen atoms on the cyclopropane ring is expected to weaken the C—C ring bonds, and it has been reported previously that activation energies for structural isomerizations of methylcyclopropanes do decrease substantially over the series cyclopropane > methylcyclopropane > 1.1or 1.2-dimethylcyclopropane. However, the present study shows that the trend does not continue beyond dimethylcyclopropane isomerization. Besides reductions in C-C bond energy, steric interactions may be increasingly important in determining the energy surface and conformational restrictions near the transition state in isomerizations of the more highly substituted methylcyclopropanes. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 38: 475–482, 2006

INTRODUCTION

To better understand the mechanisms and energetics of cyclopropane isomerizations, kinetic studies have

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been underway in this laboratory on a series of alkylsubstituted cyclopropanes, both to confirm the results of earlier kinetic work done in static reactors and to extend the range of the studies to the much higher temperatures that can be reached in shock tubes. The kinetic data obtained over the much wider range of temperatures achieved by combining the static reactor and the shock tube results allow evaluation of the Arrhenius parameters of competing isomerization channels with high precision (assuming Arrhenius behavior and no change of mechanism). In a recent study of methylcyclopropane [1], for example, we confirmed the experimental activation parameters previously reported

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for its isomerization to 1-butene and 2-methylpropene, and we found that there is a small but definite difference in activation energies for the formation of *cis*- and *trans*-2-butenes (trans > cis by 1.5 kcal/mol) [1]. This latter finding differed not only from an earlier report of an experimental study which found a much larger difference in activation energies for the production of the two 2-butenes [2], but also from a prediction based on thermochemical calculations that there should be no difference since the two 2-butenes were expected to be formed via the same transition state [3].

From a substantial number of earlier experimental kinetic studies, it has been well established that the activation energies for structural isomerizations of methyl-substituted cyclopropanes decrease with increasing methyl substitution through the series cyclopropane [4] > methylcyclopropane [1] >1,1-dimethylcyclopropane [5] and 1,2-dimethylcyclopropane [6] (see Table I). This is consistent with the expectation that increasing methyl-for-hydrogen substitution should weaken the C-C bonds of the cyclopropane ring and facilitate (stabilize) the formation of a diradical intermediate [7]. But there is experimental evidence that this trend does not continue with further methyl substitution. A report by O'Neal and Henfling [8] of a static reactor study of 1,1,2trimethylcyclopropane (tri-MCP) structural isomerization presented an E_a value similar to that reported for 1,1- and 1,2-dimethylcyclopropane isomerizations (see Table I). Furthermore, a quadruply substituted cyclopropane, 1,1,2,2-tetramethylcyclopropane, appears to deviate from this pattern even more strongly. Workers in other laboratories using either a static reactor [9] or a single-pulse shock tube [10] deduced E_{a} values that are significantly higher than the $E_{\rm a}$ reported for tri-MCP structural isomerization [8] (Table I). Also, a recent combined shock tube and static-reactor study in this laboratory covering the temperature range 656–1120 K [11], yielded an activation energy of 64.7 (\pm 0.5) kcal/mol for isomerization of 1,1,2,2-tetramethylcyclopropane to 2,4-dimethyl-2pentene over the full temperature range of the study, a value very close to that for isomerization of unsubstituted cyclopropane and more than 5 kcal/mol higher than predicted by the early thermochemical calculations [7].

In light of the previous studies of the isomerizations of methylcyclopropanes summarized above, further study of the isomerization of tri-MCP seems warranted. One issue to be clarified is the trend in activation energies. Does the activation energy lie at or below that for 1,1- and 1,2-dimethylcyclopropane structural isomerizations, leaving 1,1,2,2-tetramethylcyclopropane the curious deviant from the group trend? Or does addition of the third methyl group produce a turnaround in the trend of decreasing activation energies and fill the gap between E_a values for dimethyl- and tetramethylcyclopropanes? A second issue is whether there is any trend in the pre-exponential A factors in the rate constants for this family of reactions. From the data previously reported, no trend can be discerned; but this may be due to experimental uncertainties resulting from the relatively small temperature ranges covered in the earlier studies that made use of a single type of reactor. A third issue is the relative activation energies for the formation of isomerization products. Five are expected from tri-MCP, including cis- and trans-4-methyl-2-pentene. Will the 1.5 kcal/mol difference previously noted for the production of cis- and trans-2-butene from methylcyclopropane be reproduced with tri-MCP? The present study was carried out to answer these questions.

In the present study of tri-MCP, we have extended the kinetic experiments to a much larger range

Table IArrhenius Parameters for Structural Isomerizations of Cyclopropane and Methylcyclopropanes, as Reportedfrom Experimental Studies

Reaction	<i>E</i> _a (kcal/mol)	$\log{(A, s^{-1})}$	Reference
$\overline{\text{Cyclopropane}} \rightarrow \text{propene}$	65.0	15.2	[4]
Methylcyclopropane \rightarrow alkene isomers	64.4	15.37	[1]
1,1-Dimethylcyclopropane \rightarrow alkene isomers	61.8	15.04	[5d]
<i>cis</i> -1,2-Dimethylcyclopropane \rightarrow alkene isomers ^{<i>a</i>}	61.6	14.56	[6]
1,1,2-Trimethylcyclopropane \rightarrow alkene isomers	61.1	14.47	[8]
	63.7	15.28	This study
1,1,2,2-Tetramethylcyclopropane \rightarrow dimethyl-2-pentene	64.7	15.55	[9a]
	64.0	15.27	[9b]
	62.2	14.82	[10]
	64.7	15.47	[11]

^a Calculated from the parameters for parallel reactions in [6].

of temperatures (688–1124 K) than was covered in earlier work, by using both a static reactor and a single-pulse shock tube. In both the lower and the higher temperature regions employed in this study, the isomerization of tri-MCP leads irreversibly to the formation of five principal isomeric products: *cis*-and *trans*-4-methyl-2-pentene (4M2P), 2-methyl-2-pentene (2M2P), 2,3-dimethyl-2-butene (DM2B), and 2,3-dimethyl-1-butene (DM1B), by apparently parallel mechanisms.

EXPERIMENTAL SECTION

Materials

Tri-MCP $(99.88 \pm 0.03\%)^*$ was obtained from the American Petroleum Institute's Standard Reference Materials project at Carnegie Mellon University. All the other reagents, 4M2P (99.8%), 2M2P (99.9%), DM2B (96%), and DM1B (96%), were obtained from Wiley Organics Co. (Now ChemSampCo). These reagents were diluted with Matheson research grade (99.9999%) argon to prepare calibration and reactant samples. Matheson CP-grade (99%) cyclopropane (CP) was added to reactant mixtures as an internal thermometer. It was found by GC analysis to be 98.3% CP, 1.7% propene, with no other detectable impurities. In the shock tube runs, HP grade helium was used as the driver gas.

Apparatus

The high-temperature runs were carried out in a 2.5-cm diameter single-pulse shock tube. For the lower temperature runs, the samples were heated in one of three well-aged and conditioned 100 cm³ glass cells inserted into a constant temperature furnace. Both the shock tube and the static reactors and their operation have been described earlier [12]. A Varian model 1440-20 isothermal gas chromatograph with hydrogen flame detector, and a 3-m column of 20% polypropylene glycol saturated with AgNO₃ on 80–100 mesh Chromosorb W at room temperature was used to analyze the reactant and product samples. A Shimadzu GC-14 gas chromatograph with hydrogen flame detector, equipped with a 50 m \times 0.35 mm Petrocol capillary column, was used to separate and quantify tri-MCP and all five principal isomerization products.

Sample Preparation and Kinetic Runs

All reagents were degassed through freeze–pumpthaw cycles in a greaseless, metal vacuum line, transferred to 1- or 2-L glass storage flasks with greaseless stopcocks to which a few 5 mm diameter smooth glass beads had been added beforehand, then diluted with argon. Cyclopropane (CP) was added to most mixtures as an internal thermometer to determine the reaction temperature (see below). The tri-MCP/CP/argon mixtures were well mixed before use by applying a circular motion to the flasks. This caused the glass beads inside to orbit the inner surface of the flasks, creating turbulence to achieve the desired mixing.

The following mixture compositions (tri-MCP%:CP%) were used to measure the rates of tri-MCP isomerization:

In the static reactor: (a) 0.20:0.40; (b) 2.00:4.75, (c) 2.50:7.00, and (d) 2.00:0.00. In the shock tube: (e) 0.42:0.83; (f) 2.00:4.00, (g) 2.50:5.00; (h) 1.50:0.00; and (i) 2.00:0.00.

Reactant mixture samples ranging from 25 to 90 Torr were heated in the shock tube for $8.0(\pm 0.5) \times 10^{-4}$ s, producing reaction temperatures of 1054-1124 K and total gas pressures of 2–3 bar. In the static reactor experiments, samples of the reactant mixture ranging from 99 to 400 Torr were placed into one of the three reaction cells at room temperature. These cells were inserted into the reactor oven, which had been previously stabilized at a temperature in the range 688–745 K, for times ranging from 30 min to 5.0 h; total gas pressure during reaction was 230–1000 Torr. The reaction cells were then withdrawn from the reactor and rapidly cooled. Reaction products from both heating devices were analyzed gas chromatographically.

Mixtures were also made of individual alkenes (the expected tri-MCP unimolecular isomerization products), with each mixture containing 2.0% of one alkene plus 2.0% CP in argon, to determine whether these products would interconvert or further react under the conditions (*T*, *p*) of these experiments. Samples of these mixtures were heated to 710–714 K for 50–60 min in the static reactor and to 1074–1116 K for 8.0×10^{-4} s in the shock tube. Toluene was added to some runs on each reactant as a radical scavenger.

Calculations

The relative amounts of CP and propene, and of tri-MCP and its isomerization products, were determined

 $[\]ensuremath{^*\text{Purity}}$ levels are as indicated by the supplier, unless otherwise stated.

from GC peak heights corrected for sensitivity differences determined from calibration runs on known samples. Rate constants for $CP \rightarrow propene$, and for tri-MCP \rightarrow isomerization products were calculated assuming that both CP and tri-MCP underwent homogeneous first-order irreversible reactions. For runs on mixtures containing CP, the reaction temperature was calculated from the rate constant for $CP \rightarrow propene$ isomerization, using the well-established Arrhenius parameters $E_a = 65.0$ kcal/mol and $\log_{10}(A, s^{-1}) = 15.2$ [4]. For runs on samples that did not contain CP, the temperature was calculated from the total extent of tri-MCP isomerization to all products, using the Arrhenius parameters deduced from the runs that did contain CP (see below): $E_a = 63.7$ kcal/mol and $\log_{10} (A, s^{-1}) = 15.28.$

RESULTS AND DISCUSSION

At temperatures obtained in both the static reactor and the shock tube runs, five products of tri-MCP isomerization were identified: *cis*- and *trans*-4M2P, 2M2P, DM1B, and DM2B. An Arrhenius plot for the total isomerization of tri-MCP to all alkene isomers in the runs that contained CP for temperature determination is shown in Fig. 1. A linear least-squares regression of the data from 688 to 1124 K gave the activation parameters:

> $\log_{10} (A, s^{-1}) = 15.28 (\pm 0.12)$ $E_a = 63.7 (\pm 0.5) \text{ kcal/mol}$

The specified uncertainties are one standard deviation as calculated from the linear least squares regression. Doubling these listed uncertainties would repre-



Figure 1 Arrhenius plot for 1,1,2-trimethylcyclopropane total isomerization to all alkene products.

sent the statistical uncertainty range at the 95% confidence level. The data points from the lowest percentage mixtures are well intermingled with data points from mixtures which had initial total percentages of tri-MCP plus CP that were larger by factors of six to 10, providing experimental evidence that the results are not significantly affected by unimolecular falloff of either reaction. This point is discussed in greater detail below.

The presence of all five isomeric alkene products of tri-MCP isomerization in the product samples from even the lowest percent conversion experiments run in both the static and shock tube reactors indicates that these products are formed via parallel rather than sequential pathways. However, all were found to undergo isomerization to other isomers to a small but significant extent (2-6% consumption of reactant) when each was heated individually to the higher end of the temperature range covered in each reactor (>710 K for the static reactor and >1074 K in the shock tube). Toluene did not significantly change the extent of isomerization of the alkenes in the static reactor experiments, but it did appear to slightly increase the isomerization rates in the shock tube experiments. Baldwin and Shukla [13], studying 1,1-dimethylcyclopropane isomerization in a static reactor, noted isomerization of product alkenes and attributed this to surface-triggered formation of cationic species, followed by hydrogen or methyl shifts. They cited additional evidence for such processes from earlier isotope-labeling experiments and NMR-spectroscopic studies. Such processes could account for the slow isomerization of alkenes in the static reactor experiments of the present study, and the negligible effect of added toluene. The apparent interconversion of alkenes in the shock tube experiments, however, is an indication of the presence of some radical species in the gas phase in the higher temperature (and larger extent of tri-MCP depletion) runs, since the walls of the shock tube remained at room temperature during each shock tube run and therefore should not have catalyzed radical processes.

To obtain the Arrhenius parameters for the formation of the individual alkenes from tri-MCP, static reactor and shock tube runs were carried out on tri-MCP samples that did not contain CP, in the lower half of the useful temperature range of each reactor (<715 and <1090 K, respectively) and with short reaction times in the static reactor, to minimize further reaction of newly formed alkenes. From the product ratios for the isomerizations we obtained the Arrhenius plots as shown in Fig. 2. Linear regression of the individual data sets gives the following:

Product	$\log_{10}(A, s^{-1})$	$E_{\rm a}(\rm kcal/mol)$
cis-4M2P	14.25 ± 0.11	62.5 ± 0.4
trans-4M2P	14.77 ± 0.07	64.0 ± 0.3
2M2P	15.31 ± 0.17	66.6 ± 0.7
DM2B	14.74 ± 0.14	65.9 ± 0.6
DM1B	14.03 ± 0.23	61.0 ± 0.9

The GC analyses of tri-MCP and its isomerization products achieved good but not perfect peak separation, which produced some uncertainty in the estimation of baselines. The result could have been a slight overestimation of DM1B and both *cis*-4M2P and *trans*-4M2P, which would have lowered their apparent activation energies of formation and raised the corresponding activation energies for 2M2P and DM2B formation. Estimating the largest reasonable baseline errors and recalculating changed the above E_a values by no more than 1 kcal/mol.

Of particular interest is the difference in activation energies for the production of 4M2P isomers: E_a for the formation of the *trans* form exceeds E_a for the formation of the cis form by 1.5 kcal/mol. This is identical to what was found earlier for the production of *cis*- and *trans*-2-butene from MCP [1].

Assuming that cyclopropane isomerization is initiated by the breaking of a C–C bond in the cyclopropane ring to form a diradical transition state or intermediate, the formation of the five principal alkene products can be understood from Fig. 3. Breakage of the C–C bond between the singly substituted and the unsubstituted carbon atoms would not be expected to lead to a major product as there is no H atom to migrate from the central carbon of the resulting diradical.

From the observed distribution of products from each run, the total amounts of the three methylpentenes range from 2-4 times that of the two dimethylbutenes. This echos observations made by O'Neal and Henfling in their study [8] and is consistent with the expectation that the C-C bond between the most highly substituted carbon atoms (1 and 2) would require the least energy to break and therefore would break most frequently. Once a diradical is formed from cleavage of either the C1-C2 or the C1-C3 ring bond, the transfer of an H atom to the doubly substituted C1 carbon is favored over an H atom transfer to the singly substituted C2 or the unsubstituted C3 carbons: the ratio [4M2P]/[2M2P] is 3.8 at 702 K but drops to 1.0 at 1122 K; and the ratio [DM1B]/[DM2B] is 6.1 at 702 K and drops to 0.8 at 1122 K. Thus, the preference for H atom migration to the more highly substituted carbon of the diradical is clearly observed in the lower temperature static reactor data, but is not significant at the much higher temperatures reached in the shock tube.

As mentioned in the introduction, the isomerizations of CP and the variously substituted methylcyclopropanes follow a pattern of decreasing activation energies with increasing substitution of Hs by CH₃ groups (Table I), through the dimethylcyclopropanes. The E_a values descend from a high of 65.0 kcal/mol for structural isomerization of CP to a low of 61.8 kcal/mol for 1,1-dimethylcyclopropane and 61.2–62.3 kcal/mol for *cis*-1,2-dimethylcyclopropane.



Figure 2 Arrhenius plots for the formation of different products from the thermal isomerization of tri-MCP. The plots for the different products have been offset by different *Y*-axis increments for clarity: n = 6 for DM1B, 8 for DM2B, 10 for 2M2P, 12 for *cis*-4M2P, and 14 for *trans*-4M2P.



Figure 3 Formation of likely diradical intermediates and the observed product alkenes from tri-MCP.

This trend might lead one to expect an overall activation energy for the structural isomerization of 1,1,2trimethylcyclopropane in the range 59–61 kcal/mol. Indeed, earlier experimental evidence supported by the theory seem to support that expectation: O'Neal and Henfling's 61.1 kcal/mol E_a and the values they estimated from transition state calculations for the formation of methylpentenes and dimethylbutenes, 59.4 and 61.6 kcal/mol, respectively [8].

The activation energy of $63.7(\pm 0.5)$ kcal/mol determined for the unimolecular isomerization of tri-MCP found in the present study is more than two standard deviations higher than the previously measured and predicted values [8]. The value determined for $\log_{10}(A, s^{-1})$ in the present study, 15.28 (±0.12), is also substantially higher than the value 14.47 previously reported [8]. However, if actual rate constants from the two studies are compared, our measured rate constants at 700-755 K are larger than those of O'Neal and Henfling [8] by only a factor of 1.06–1.11. which represents full agreement within experimental uncertainties. The observed differences in Arrhenius parameters may be due to small systematic errors in the earlier study which covered a much narrower temperature range than the present work.

In examining the trends evident in Table I, it is important to consider whether the differences in E_a are statistically significant. Each of the earlier published reports of the activation parameters of a methylcyclopropane isomerization (those summarized in Table I) included uncertainty estimates. In some cases, these were the statistical standard deviations obtained through linear least-squares data regressions; in other cases, they represented the result of a thoughtful assessment by the authors of the probable error limits of their experiments. Considering the different bases for error estimation, we have not included uncertainty estimates with the entries in Table I. The key consideration, however, is whether the value of E_a reported here for tri-MCP isomerization is really significantly different from that reported earlier [8], beyond experimental uncertainties. We believe that the following analysis establishes that it is.

In the experiments on tri-MCP reported earlier [8] and in the present study, the dominant source of experimental error is probably the measurement of the reaction temperature. In the earlier study, the accuracy of the temperature measurements depended on the calibration of a mechanical or electrical device and the maintaining of total thermal equilibrium at that temperature throughout the reaction cell. In the experiments reported here, the accuracy of the measurement of reaction temperature depended upon the accuracy of the activation parameters for the CP-topropene reaction and the assumption that the reaction was proceeding at the high-pressure limit under our experimental conditions. The Arrhenius parameters deduced in the two laboratories give virtually identical rate constants in the temperature range of the static reactor experiments; where $\log_{10}(k, s^{-1}) = -4.00$, the temperature is expected to be 722 K according to the O'Neal and Henfling parameters [8], and 723 K from the parameters deduced in this study. But contrast the situation at the higher temperatures of the shock tube experiments: $\log_{10}(k, s^{-1}) = 3.00$ is expected to occur at 1164 K from the O'Neal and Henfling parameters [8] and 1134 K from the parameters of this study, a substantial difference of 30 K. Could the present shock tube study be that much in error?

It has been well established [14] that gas-phase reactions are more likely to be affected by unimolecular falloff as temperature increases, assuming the reaction rates are compared at constant pressure. Also, the smaller the molecule, the higher the pressure below which falloff becomes important, because of the smaller number of active vibrations. Thus, one would expect that if either the tri-MCP or the CP isomerization was significantly slowed by falloff, the reduction in reaction rate would be greater for CP isomerization. The temperature calculated from extent of CP isomerization would then be too low, and the resulting Arrhenius plot for tri-MCP isomerization would be too steep, giving erroneously large values of $E_{\rm a}$ and A. But to give a temperature error of 30 K, the CP reaction would have to be proceeding at only half the high-pressure rate. Thus, if the previously reported Arrhenius parameters for tri-MCP isomerization were correct, then for the present study to have produced the parameters we obtained would have required that both reactions proceeded at the high-pressure limit in the static reactor, but that the rate of the CP reaction dropped to half its high-pressure value in the shock tube while the tri-MCP reaction proceeded at its high-pressure limit. This is an implausible set of circumstances, especially since the partial pressure of organic species (tri-MCP plus CP) in the shock tube experiments was varied by a factor of 6 with no resulting evidence of changes in the ratio of $k_{tri-MCP} : k_{CP}$.

CONCLUSIONS

The identities and the relative amounts of five principal thermal isomerization products of 1,1,2trimethylcyclopropane have been determined over a wide range of temperatures, 688-1124 K. The products are likely formed from two diradical intermediates produced by competitive breaking of two of the C-C bonds of the cyclopropane ring (Fig. 3). The five alkene products can interconvert, albeit slowly, under conditions covered in this study, complicating absolute determination of their individual rates of production. However, this complication was minimized by considering product production ratios in only the lower temperature runs in each reactor, runs in which extents of tri-MCP depletion were low. In this study, estimates of the activation parameters of individual isomerization channels made from the lowest percentage conversion experiments are consistent with expectations based on the relative ease of rupture of the differently substituted C-C bonds of the tri-MCP ring (see earlier discussion).

From the rate constants at different temperatures for the structural isomerization of tri-MCP \rightarrow alkenes, kinetic parameters at the 95% confidence level (twice the standard deviation) been determined to be $E_a = 63.7$ (± 0.9) kcal/mol, and $\log_{10} (A, s^{-1}) = 15.28(\pm 0.24)$. This E_a value is significantly higher than E_a values reported for 1,1- and 1,2-dimethylcyclopropane isomerizations [5,6]. We conclude that E_a reaches its lower limit at dimethylcyclopropane isomerization, then increases upon further addition of methyl substituents.

The trend of decreasing E_a with increasing methylfor-hydrogen substitution in methylcyclopropanes is the expected result of weakening the C—C ring bonds between the more highly substituted carbon atoms. The turnaround to increasing E_a is likely the result of increased steric interactions (repulsions) between methyl substituents that raise the enthalpy of the diradical as it approaches the transition state along the reaction coordinate. In contrast, the pre-exponential factors for overall structural isomerization of all the methylcyclopropanes listed in Table I appear to group (within margins of error) at $\log_{10} (A, s^{-1}) = 15.2(\pm 0.3)$, showing no particular trend with increasing substitution. This indicates that methyl-for-hydrogen substitution, except for changing the height of the enthalpy barrier, does not cause significant changes in the structure of the transition state or the entropy of activation in these isomerizations.

Activation energies for the formation of the trans and cis isomers of 4-methyl-2-pentene differ by 1.5 kcal/mol (*trans* > *cis*). This difference is identical to the one found earlier for the production of *cis*- and *trans*-2-butene from methylcyclopropane.

Isomerizations of cyclopropane and its alkylsubstituted derivatives serve as important test reactions for the development of computational methods for estimating transition state enthalpies, and for assessing probable trajectories for cyclopropane structural isomerizations and stereomutations [15]. The reversal in the decline of E_a with increasing methyl-for-hydrogen substitution reported here provides an important opportunity for testing and further improving the predictive accuracy of the computations. Also, tables of thermochemical data that have been used to analyze transition states and predict reaction rates [16] should be updated to correctly account for the trends and differences in activation energies noted here.

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