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# On the Question of Carbonium Ions as Intermediates over Silica–Alumina and Acidic Zeolites

G. M. KRAMER, G. B. MCVICKER, AND J. J. ZIEMIAK

*Corporate Research Science Labs, Exxon Research and Engineering Company, Route 22 East, Clinton Township, Annandale, New Jersey 08801*

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Activation energies for the isomerization of an equilibrated mixture of 2-methylpent-1-ene and 2-methylpent-2-ene to several isomers with an ultrastable Y catalyst have been found to correspond closely with the barriers to the rearrangement of the same "postulated" carbonium ions in superacids. This provides evidence for relatively stable carbonium ions as reaction *intermediates* on this solid acid. The same rearrangements with a conventional amorphous $SiO_2$–$Al_2O_3$ catalyst involve distinctly different barriers and are more indicative of the presence of surface alkoxy compounds as intermediates. With these catalysts it is proposed that rearrangements may occur through polar (cationic-like) transition states. © 1985 Academic Press, Inc.

Solid acids have long been used as catalysts in the petroleum and chemical industries. Since the midthirties amorphous silica–alumina catalysts have been used in cracking heavy petroleum distillates to gasoline (*1, 2*). The process has often been considered as one involving carbonium ions as real intermediates (stable species on a reaction coordinate diagram) (*3–14*), although the possible occurrence of polar complexes (sometimes equated to carbonium ions) (*15, 16*), free radicals, or radical cations as alternate participants has also been raised on various occasions (*17*).

The existence of carbonium ions as intermediates has been assumed as there is a general analogy between certain reactions occurring over the solid acid catalysts, albeit while hot (usually about 500 to 900°K), and those found with strong mineral acids at much lower temperatures. Thus amorphous silica–alumina is known to affect double-bond and skeletal rearrangement of olefins, alkyl disproportionation reactions of substituted aromatics and polymerization reactions (*2, 18–22*). In addition, paraffinic cracking products often contain higher-than-equilibrium ratios of iso-paraffins/n-paraffins and this has been taken as evidence for the incursion of carbonium ion cracking processes (*2*).

Mechanistic studies of the reactions of low-molecular-weight paraffins also indicate the occurrence of chemistry attributable to carbonium ions under a variety of experimental conditions. These include observing the extent of isotopic exchange, racemization, isomerization, and cracking as well as the effect of initiators or carbonium ion precursors upon the complex reactions (*15, 16, 23–27*). The copious literature leaves little doubt that carbonium ion-like processes are occurring but the nature of the ionic species are far from clear.

Problems with carbonium ion formalism arise in part from the fact that the catalysts often exhibit variable reactivities for reasons which are difficult to quantify. Thus the mode of pretreating a catalyst, its exposure to $H_2O$ vapor, and other factors greatly influence activity and selectivity patterns. Interpretation problems are also related to the detection of reactions which are not consistent with normal carbonium ion behavior. One example is found in studies of the extent of hydrogen exchange of a

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series of tertiary alkanes over an amorphous silica–alumina catalyst at 425°K (*16*). Here it was found that in addition to exchange occurring at sites contiguous to the cationic carbon, it sometimes also took place at this carbon atom. In addition, proton exchange with 2-methylheptane over the same catalyst was reported to have occurred at positions in the alkyl chain far from the tertiary site, and under conditions at which alkyl migration was not occurring.

While it may be possible to reconcile these observations with carbonium ion theory, they lead to questions about the nature of the polar hydrocarbon species and of the active site involved in the exchange reactions.

There are additional reasons for questioning the role of carbonium ions as unique or sole reactive intermediates in the conversion of hydrocarbons over amorphous silica–alumina catalysts. One is that under typical catalytic cracking conditions with such catalysts the products of alkane cracking contain large quantities of light olefins and lesser amounts of their corresponding alkanes, with the olefins being at essentially thermodynamic equilibrium while the paraffin distribution is generally far removed from equilibrium. If one attributes the formation of both olefinic and paraffinic products to a single set of equilibrating carbonium ions, then one has to propose that the intermolecular hydride transfer reaction leading to alkanes is slow and responsible for the kinetically controlled formation of the alkanes with high iso/normal ratios. This is problematic since secondary ions by all accounts are believed to be more reactive than their tertiary isomers and if they are, carbonium ion theory would lead to the expectation of a product distribution which would be at odds with that found.

These concerns have been raised anew in a recent paper which reported that isobutane was not isomerized to n-butane over many solids often suggested as being quite acidic (*28*). In that paper it was noted that the kinetics and product distributions obtained over alumina, chloridized and fluoridized alumina, and amorphous silica–alumina indicated that radical cations and not carbonium ions were likely intermediates over these acids. Particularly striking was the failure of these materials to support the formation of intermediates which would take part in intermolecular hydride transfer reactions.

In complementary studies it was also found that 3-methylpentane tended to undergo cracking rather than isomerization reactions with the same set of solid acids. While a measurable isomerization of 3-methylpentane does occur, at temperatures of the order of 773°K which were required to obtain low but meaningful conversions, the products were again indicative of being mainly derived from radical cations rather than from carbonium ions.

The preceding behavior was contrasted by that of an ultrastable Y zeolitic catalyst in the protio form which readily isomerized isobutane to n-butane and which caused predominant isomerization rather than cracking of 3-methylpentane. Conversion of isobutane appears to be proceeding through a carbonium ion reaction whose chain length could be estimated.

To probe the acidity of the various solid acids in more detail, a study was made of the ability of the acids to isomerize 2-methylpent-2-ene. Rearrangement of this compound can be thought of as proceeding through the intermediacy of cationic transition states or intermediates to various isomers. While the relative rates of conversion to isomers requiring a skeletal rearrangement of the carbon framework as opposed to those obtained by only proton or 1,2 hydride migrations can be used to define a useful acidity scale for acid catalysts (*29*) experimental activation energies for some of the processes taking place provide a strong indication of the presence of relatively free carbonium ions as real intermediates over ultrastable Y. The situation is not as clear with amorphous silica–alumina where apparent activation energies vary considerably and the data lend themselves to varied interpretation. In this paper the energetics over ultrastable Y and amorphous silica–alumina are contrasted and a hypothesis is proposed that the major route to rearrangement with amorphous silica–alumina involves the interconversion of alkoxy groups through cationic transition states rather than through "stable carbonium ion intermediates."

## EXPERIMENTAL

Two different experimental procedures were employed in these studies. This was necessitated because the catalysts, and the ultrastable Y catalyst in particular, suffer substantial losses in activity during the course of a catalytic run. The first procedure, A, involved a series of rate measurements at increasing temperatures followed by a single determination at a lower temperature to qualitatively assess deactivation during the run. The second method, B, used a sequence of rate measurements starting with the maximum temperature to be employed throughout the experiment followed by determinations at a series of decreasing temperatures. From the minimum the series was continued in ascending fashion until the initial maximum temperature was once again reached.

For both procedures, A and B, the isomerization of 2-methylpent-2-ene was conducted by flowing a helium stream containing 7 mol% olefin at 101 kPa at a rate of 150 $cm^3$/min over 1 g of catalyst contained in a 22 $cm^3$ stainless-steel reactor. In several cases hydrogen was used as the carrier gas instead of helium in an attempt to suppress the formation of inhibitors but no major rate differences were observed. The reactions were carried out between 323 and 473°K over an ultrastable Y catalyst and at temperatures up to 523°K with a conventional amorphous silica–alumina catalyst.

Catalysts were pretreated in flowing helium for about 1.0 hr at 773°K before use. Products were analyzed with an on-line Varian 3700 gas chromatograph containing a 50-m capillary column which was able to resolve all 17 hexene isomers. The capillary column was coated with SP-2100. The ultrastable Y and amorphous silica–alumina catalysts had surface areas of 770 and 350 $m^2$/g, respectively, as determined by the BET method employing nitrogen (see Ref. (*28*) for complete catalyst specifications).

## RESULTS AND DISCUSSION

The rearrangement of 2-methylpent-2-ene can be thought of as occurring by the formal protonation of the olefin followed by the isomerization and eventual deprotonation of reaction intermediates. The catalytic intermediates might be relatively free carbonium ions or alkoxy groups bound to silicon or aluminum atoms on the surface of the solid acid.

The question of the nature of the intermediates can be probed by determining the energetics of the rearrangements. If these species are essentially unsolvated and stable carbonium ions, the activation energy for the isomerization of the reactant and 2-methylpent-1-ene with which it rapidly equilibrates, to their isomers, 4-methylpent-2-ene and 3-methyl-pent-2-ene, would be expected to approach those found in the analogous ionic rearrangements in super acids at subambient temperatures. If not, differences should occur.

Several Arrhenius plots for the isomerization of 2-methylpent-2-ene to 4-methylpent-2-ene over ultrastable Y are shown in Fig. 1. Also shown is a corresponding set for the conversion to 3-methylpent-2-ene. Each set is seen as a pair of lines with slightly varying activation energies. The activation energies vary because they have been obtained for catalysts having slightly different activities. This activity difference arises in part from the experimental procedure employed (A or B) and in part from slow deactivation occurring throughout the course of each experiment.

In spite of these problems, deactivation throughout the course of a sequence of measurements is not severe enough to pre-

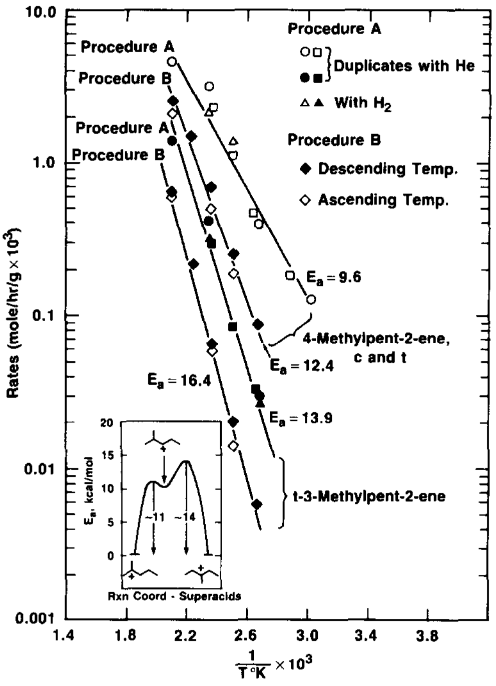


FIG. 1. Arrhenius plot for isomerization of 2-methylpent-2-ene over ultrastable Y.

vent the determination of linear Arrhenius plots from which mechanistically useful conclusions may be inferred.

A similar set of graphs have been obtained for the same isomerizations over an amorphous silica–alumina catalyst. Figure 2 shows the Arrhenius graphs obtained via procedure B. It may be noted that the activation energies obtained via this method are about 3 to 5 kcal/mol greater than those found using procedure A. Of more importance, however, is the fact that the activation energies obtained via either procedure are significantly different from those found with the zeolite and that the difference in the barriers for processes leading to double bond and methyl group shifts is about the same irrespective of the procedure followed. This latter difference appears to depend on the catalyst and will be used to suggest that there probably is a fundamental difference in the nature of the intermediates present over the ultrastable Y and amorphous silica–alumina catalysts.

The difference in activation energies is reflected in catalyst selectivity, i.e., in the relative rate of conversion of the reactant into its isomers (see Table 1). At a given temperature the 3-methylpent-2-ene to 4-methylpent-2-ene rate ratio remains relatively constant for each catalyst even though catalyst activity declines with time. Hence the loss in activity appears to be due to a general diminution of all catalytic sites rather than to the selective loss of sites which preferentially generate a particular product.

Before considering the activation energies in more detail, it may be noted that the activity of the "lined-out" catalysts shown in Table 1 differ grossly from the initial activities observed with these catalysts. Initially ultrastable Y is more active than the amorphous silica–alumina but its reactivity declines drastically during its conditioning period. In the conditioning period the zeolite catalyst generates about four times

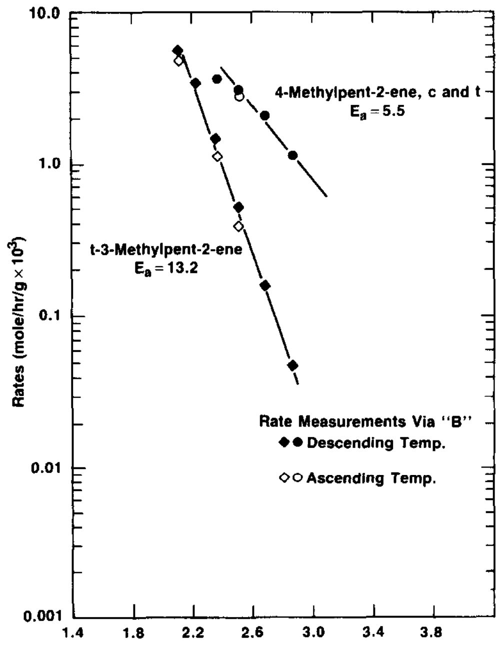


FIG. 2. Arrhenius plot for isomerization of 2-methylpent-2-ene over $SiO_2$, 87-$Al_2O_3$, 13.

TABLE 1

| Catalyst temperature (°K) | Ultrastable Y | | Amorphous silica–alumina | |
|---|---|---|---|---|
| | Rate[a] (m/hr/g × $10^3$) | Selectivity ratio[b] | Rate (m/hr/g × $10^3$) | Selectivity ratio |
| 473 | 9.89 | 0.25 | 18.3 | 1.76 |
| 448 | 8.12 | 0.14 | 13.7 | 0.98 |
| 423 | 6.93 | 0.094 | 11.9 | 0.41 |
| 397 | 6.07 | 0.077 | 10.4 | 0.16 |
| 374 | 5.49 | 0.064 | 8.37 | 0.075 |
| 348 | | | 6.27 | 0.043 |
| 398 | 5.88 | 0.073 | 9.52 | 0.13 |
| 423 | 6.35 | 0.087 | 11.0 | 0.32 |
| 473 | 9.31 | 0.27 | 17.5 | 1.41 |

[a] The rate is for the conversion of 2-methylpentenes to all products. Measurements were made by method B.

[b] The selectivity ratio is the ratio of the rate of forming t-3-methylpent-2-ene to that of forming *cis*- and *trans*-4-methylpent-2-enes.

more coke than the amorphous silica–alumina.

Two of the lines in Fig. 1 relate to the isomerization of 2-methylpent-2-ene to 4-methylpent-2-ene and 3-methylpent-2-ene as determined by procedure A. The rates are representative of steady-state behavior over a stabilized or "lined-out" catalyst. Rates were obtained by following a specific experimental procedure which leads to reproducible results, even though the catalyst undergoes deactivation prior to "line-out." Procedure A involved: (1) bringing the reactor to temperature, (2) flowing the olefin in helium over the catalyst for 10 min and making rate measurements after this time, (3) heating to the next temperature while still flowing helium, and (4) reintroducing the reactant for another rate determination. Following this procedure the catalysts generally exhibited a high and variable initial activity which rapidly decreased during the first 10–20 min on feed. After this time, rates increased upon heating, linear Arrhenius plots were obtained and the catalysts were considered to be "lined-out." Figure 1 shows data obtained from two experiments carried out this way and for a third where hydrogen was used instead of helium. Hydrogen had little effect on the rates displayed by a steady-state catalyst.

### *Reactions with Ultrastable Y Parallel Behavior in Super Acids*

The activation energy for the double-bond migration determined by procedure A is 9.6 kcal/mol while that for the process leading to the methyl shift is 13.9 kcal/mol. The same processes when measured following procedure B exhibit energy barriers of 12.4 and 16.4 kcal/mol, respectively. Before comparing these results with ionic behavior in super acids it is important to consider method B in some detail. Under this method the catalysts were initially aged at 473°K for 1 hr while being purged with a helium/2-methylpent-2-ene stream. This pretreatment deactivates the catalysts to an essentially steady-state level of activity. After completing a rate measurement at this temperature, the feed was stopped and the catalyst allowed to cool to 448°K while being flushed with helium. A 10-min isomerization experiment at 448°K was made and the cycle was then repeated at successively lower temperatures. After arriving at the lowest temperature, measurements were made at a series of ascending temperatures until the initial temperature point was reached.

An indication of the fact that ultrastable Y is deactivating at a slow rate is obtained by comparing the rates of forming isomers like t-3-methylpent-2-ene and *cis*- and *trans*-4-methylpent-2-ene at equivalent temperatures reached during the falling and rising portions of the cycle. These rates decrease by about 5–10% during the course of the experiment.

In addition, the ratio of the rates of forming these isomers which reflects the inherent ability of the catalyst to cause a methyl shift as opposed to a double-bond migration also declines slightly. The implication of the rate and rate ratio determinations is that there is a slow drop in the concentration of active intermediates but that the nature of the intermediates is essentially unchanged throughout the experimental cycle.

The insert in Fig. 1 shows the reaction coordinate diagram for the rearrangement of a tertiary 2-methylpentyl cation to a tertiary 3-methylpentyl ion in super acid systems (*30*). For the super acid the 1–2 hydride shift which converts a tertiary ion to a secondary is found to have an energy barrier of about 11 kcal/mol. On the ultrastable Y catalyst the corresponding activation energy varied from 9.6 to 13.9 kcal/mol depending on the procedure followed.

The barrier to the methyl migration interconnecting the secondary ions entails a further 3 to 4 kcal/mol with the super acid and similar increments of 4.3 and 4.0 kcal/mol were observed following procedures A and B, respectively. The apparent activation energies are therefore indicative of the presence of relatively free, stable alkyl cations, as intermediates on the surface of ultrastable Y.

These results are consistent with a mechanistic study of the isomerization of isobutane over this catalyst. There it was concluded that after oxidative initiation a chain reaction involving intermolecular hydride transfer between the hydrocarbon and carbonium ions occurred.

### *Amorphous Silica–Alumina Behaves Differently*

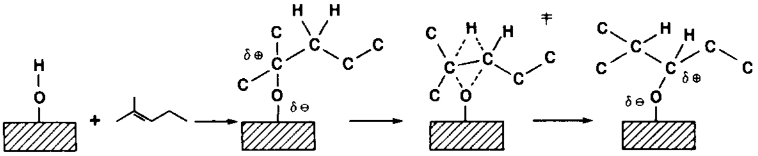
The behavior of 2-methylpent-2-ene with amorphous silica–alumina is much different (Fig. 2). In this case the activation energies depend somewhat more than the zeolite on the procedure followed. Still, the values are such as to make it clear that the system is behaving in a qualitatively different way than the zeolitic catalyst.

Following method A the barrier to the double-bond shift yielding 4-methylpent-2-ene was found to be 1.9 ± 1 kcal/mol and to the methyl shift yielding 3-methylpentenes was found to be 8.2 ± 1 kcal/mol. These values are raised significantly to 5.5 and 13.2 kcal/mol following the deactivating procedure B. The incremental barrier to the methyl shift is therefore 6.3 kcal/mol using procedure A and 7.7 kcal/mol using procedure B.

The first point to be made regarding these values is that they are inconsistent with those obtained while rearranging relatively free ions in super acid solutions. The data themselves are about as internally consistent as those found with the ultrastable Y in that the rates and rate constants obtained via method B also decrease by about 5–10% throughout the cyclic experiment.

These data lend themselves to varied interpretation. We have a preference for the hypothesis that they relate to the barriers for the interconversion of alkoxy intermediates on the surface of the amorphous solid acid but have no proof which rules out the possible existence of a low concentration of short-lived alkyl cations as reaction intermediates. The inferential evidence, particularly from the inability of amorphous silica–alumina to catalyze the isomerization of isobutane to n-butane, is however, suggestive of the absence of relatively free secondary cations on its surface.

In our hands, this catalyst has been found to cause the isomerization of 3-methylpentane to 2-methylpentane, but only at high temperatures where cleavage to radi-



SCHEME 1

cal-type products is proceeding at least as rapidly. This might be interpreted as evidence of the presence of a carbonium ion intermediate but might equally be due to the reaction of a polar, cationic-like, organic species bound to the surface, with a gas phase or adsorbed alkane. Such a species would represent an alkoxy compound which could lead to the rearrangement of olefins by a mechanism such as is outlined in Scheme 1.

In Scheme 1 a possible mechanism is shown for the conversion of a tertiary 2-methylpentylalkoxy intermediate to a sec-2-methyl-3-pentyl isomer. It is assumed that this rearrangement is the rate-determining step and entails the formation of a transition state in which both C–O and C–H bonds are being broken and made. The relatively low activation energy for the "double-bond shift" could be due to the concertedness of the process which negates the requirement of forming a free secondary cation. It would also seem reasonable that the transition state leading to the methyl shift from the sec-alkoxy compound would be energetically more demanding as it should require the development of considerable positive charge at the 3-carbon before the group begins to move. Thus the incremental 6 to 7 kcal/mol required for the methyl shift may be taken as supportive of this hypothesis.

A plausible alternative view of the slow step in the process might be the protonation of olefins coupled with the generation of C-surface bonds which would form alkoxy compounds on the catalyst surface. The principle of microscopic reversibility would then require deprotonation to be the slow step in olefin isomerization with this catalyst. This proposal could account for the energetics of the isomerization to 4-methylpent-2-ene but the additional energy required for the methyl shift to 3-methylpentenes is not easily rationalized on this basis.

## SUMMARY

A close correspondence has been found between the apparent activation energies for double-bond and methyl migrations over ultrastable Y with those obtained in super acids for ionic rearrangements. The data provide evidence for the presence of relatively "free" alkyl cations on this zeolite.

In marked contrast, the rearrangement over an amorphous silica–alumina solid acid follows a different energetic path which is hypothesized as being more indicative of the presence of surface alkoxy compounds as reaction intermediates.

In response to requests from several reviewers of this paper, Fig. 3 has been added to the text in an attempt to clarify the terminology which has been employed. The diagram lists the heats of formation of carbonium ions and several hypothetical and unionized precursors at points D and A. When the latter are contacted with solvent they become solvated to varying extents and when the interaction reaches point B ionization occurs. Ionization may be either an exothermic or endothermic process and the illustration pertains to the latter case.

Reactions involving polar intermediates lying between A and B correspond to what we believe occurs over the $SiO_2$–$Al_2O_3$ catalyst but it is admittedly difficult to distinguish them from some carbonium ion reactions which could occur by species lying in

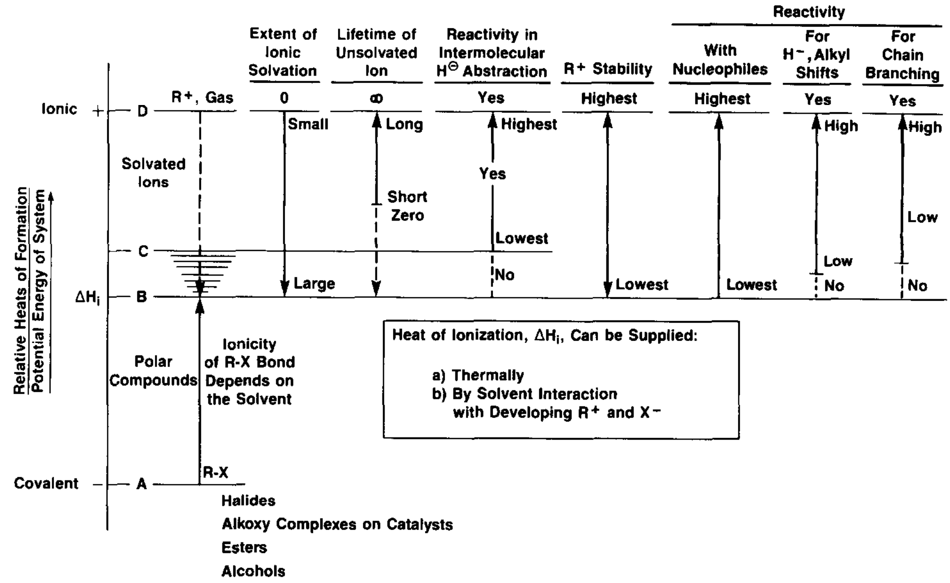


FIG. 3. Characterizations of carbonium ions and polar precursors.

region B–C. Species lying between C and D correspond to those we call relatively stable carbonium ions. The more closely they approach D the longer is their lifetime and the more likely are they to be observable by procedures like NMR spectroscopy. In the limiting case, i.e., under vacuum the ions are unsolvated with essentially infinite life.

Ions in the C–D range have the ability to participate in intermolecular hydride transfer reactions as well as all of the reactions which the more heavily solvated ions (B–C) and their polar precursors undergo. The relatively stable carbonium ions are distinguished from the species lying between A and C because of the inability of the latter to take part in this characteristic reaction.

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