Artigo

GAS-PHASE SOLVOLYSIS TYPE REACTIONS OF SiCl₃⁺ CATIONS[#]

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Gas-phase $SiCl_3^+$ ions undergo sequential solvolysis type reactions with water, methanol, ammonia, methylamine and propylene. Studies carried out in a Fourier Transform mass spectrometer reveal that these reactions are facile at 10^{-8} Torr and give rise to substituted chlorosilyl cations. *Ab initio* and DFT calculations reveal that these reactions proceed by addition of the silyl cation to the oxygen or nitrogen lone pair followed by a 1,3-H migration in the transition state. These transition states are calculated to lie below the energy of the reactants. By comparison, hydrolysis of gaseous CCl_3^+ is calculated to involve a substantial positive energy barrier.

Keywords: silicylium ions; gas-phase; solvolyses.

INTRODUCTION

Silicylium ions, R_3Si^+ (R = alkyl), are ubiquitous fragment ions in the mass spectra of organosilanes[1] but their characterization as free ions in condensed phases has been a long standing challenge.[2] The gas-phase ion chemistry of R_3Si^+ ions has been studied in some detail[3] and they are known to be powerful electrophiles that can readily promote reactions by addition-elimination type mechanisms.[4]

Our group has studied several aspects of the gas-phase ion/molecule reactions of the tetralkoxysilanes[5-8] because of the role that these substrates play as precursors of both, sol-gel processes relevant to functional materials, and CVD processes relevant to microelectronics. Silicon tetrahalides, and particularly the fluoro and chloro derivatives, are also known to be intimately related to CVD processes and $SiCl_4$ and the hydrolysis and ammonolysis of the neutral substrates have been characterized both experimentally[9] and theoretically.[10] The fragment ions from these silicon halides have also been observed to undergo facile hydrolysis in the gas-phase,[11,12] and detailed studies with SiF_3^+ in the gas-phase have shown that this cation can react in the gas phase through an addition-elimination mechanism with a number of n-donor bases that results in the elimination of HF.[13,14]

Because of the differences in Si-F and Si-Cl bond energies and the likelihood that $SiCl_3^+$ could display a distinct chemistry from SiF_3^+, as illustrated for CF_3^+ and CCl_3^+,[15] we undertook an extensive investigation of the gas-phase ion chemistry of $SiCl_3^+$. In this paper, we report an experimental and theoretical characterization of some simple gas-phase solvolysis type reaction of the $SiCl_3^+$ and possible implications of this chemistry in gas-phase processes.

EXPERIMENTAL

Experiments were carried out in a custom made FT-ICR spectrometer whose original design was first reported in this journal.[16] This spectrometer typically operates at a fixed magnetic field of 1.0 T provided by a 9 inch electromagnet that operates exclusively under internal ionization and is interfaced to an IonSpec Omega Fourier Transform Data System.

The cell of the spectrometer is a modified near-cubic 15.6 cm³ one-region cell in which center holes have been drilled on both transmitter plates to allow for laser irradiation of the ion cloud. The temperature of the cell under normal operating conditions (with the ionizing filament turned on) is typically 333 ± 5 K as measured previously with a Pt wire thermometer located near one of the transmitter plates.

$SiCl_3^+$ ions were generated from $SiCl_4$ by electron ionization at 20 eV at pressures in the 1 to 3×10^{-8} Torr range as monitored by a nude ion gauge located just before the turbomolecular pump. The reactivity of the $SiCl_3^+$ ions was followed after ejection of all unwanted ions from the ICR cell with a combination of short radio-frequency pulses. In most cases, isolation of the $SiCl_3^+$ was carried out maintaining the full isotopic composition. Isolation of the m/z 133 ions, corresponding to $Si^{35}Cl_3^+$ ions, revealed that the isotopic composition is recovered through chloride abstraction reactions with the parent neutral. Thus, studies initiated by isolation of $Si^{35}Cl_3^+$ ions proved to be of limited advantage under our experimental conditions.

The additional neutral reagents were introduced in the cell through leak valves to a final pressure of 5 to 6×10^{-8} Torr. Facile hydrolysis of the $SiCl_3^+$ ions was observed even in the presence of trace amounts of H_2O in the vacuum system and in spite of extensive bake-out procedures of the high vacuum system.

All the reagents, quoted to have 99.9% purity, were commercially available and were used without further purification. All samples were repeatedly distilled under vacuum prior to introduction in the cell.

Ab initio calculations

Theoretical calculations were carried out with the Gaussian 03 suite of programs.[17] Initial calculations for the structure and energy of reagents, products and transition states were carried out at the B3LYP/6-311+G(d,p)/6-311+G(d,p) level theory and vibrational frequencies corrected by a constant factor of 0.9679 to estimate the zero-point energies.[18] Calculations for the simplest reactions were also performed at the MP2/6-311+G(d,p)/6-311+G(d,p) level with vibrational frequencies corrected by a constant factor of 0.9523 to estimate the zero-point energies.[19] All transition states were characterized by

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a single imaginary frequency and intrinsic reaction coordinate (IRC) calculations were carried out to characterize the connection between reaction intermediates and transition states.

A more extensive comparison of theoretical methods was pursued for the hydrolysis reaction of SiCl$_3^+$. Thus, additional calculations were carried out using the M05-2X functional with the 6-311+G(d,p) basis set as well as the highly correlated *ab initio* method CCSD(T)/6-311+G(d,p)//MP2/6-311+G(d,p) with vibrational frequencies corrected by a constant factor of 0.9639 to estimate the zero-point energies.[19]

RESULTS AND DISCUSSION

Hydrolysis of SiCl$_3^+$

Gas-phase SiCl$_3^+$ cations react rapidly with H$_2$O through successive hydrolysis reactions represented in Equation 1 and shown in Figure 1.

$$Cl_{3-x}Si(OH)_x^{\oplus} \; (x = 0 - 2) \; + \; H_2O \; \longrightarrow \; Cl_{2-x}Si(OH)_{x+1}^{\oplus} \; + \; HCl \quad (1)$$
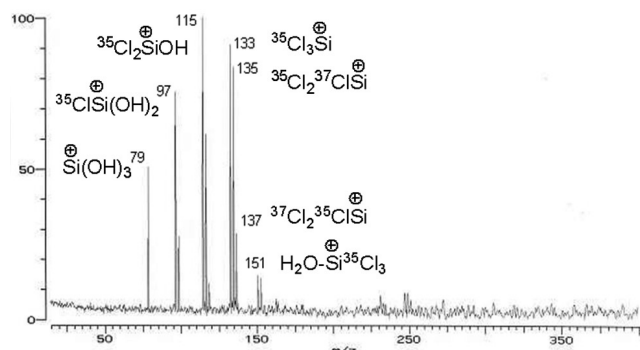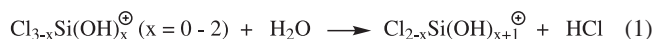

Figure 1. *Mass spectrum obtained in the FT-ICR spectrometer after 370 ms trapping time revealing the sequential hydrolysis of SiCl$_3^+$ ions. Spectrum obtained from a mixture containing nominal pressures of 1.36 x 10^{-8} Torr of SiCl$_4$ and 0.64 x 10^{-8} Torr of H$_2$O*

Although no attempts were made at measuring absolute rate constants because of the difficulty in measuring the absolute pressure of water in the system, the kinetics shown in Figure 2 reveal that these reactions must proceed at rates close to the collision limit.
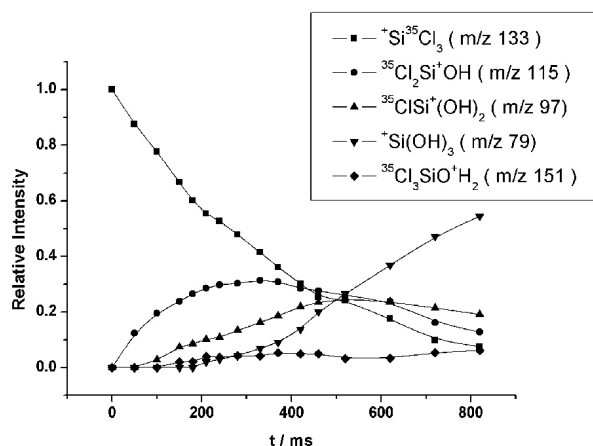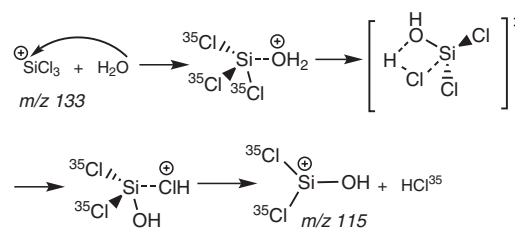

Figure 2. *Relative intensities of the Cl$_{3-x}$Si(OH)$_x^+$ (x = 0 -3) ions as a function of reaction time in an experiment carried out with a mixture containing nominal 1.36 x 10^{-8} Torr of SiCl$_4$ and 0.64 x 10^{-8} Torr of H$_2$O*

By analogy with the reactions previously studied for SiF$_3^+$,[12,14] the likely mechanism for reaction 1 for SiCl$_3^+$ is represented in Scheme 1.

Scheme 1

The proposed mechanism is confirmed by theoretical calculations that reveal that the energy profile of reaction 1 displays the usual double-well potential energy diagram of many gas-phase ion/molecule reactions.[20] Figure 3 shows the calculated energy diagram for the gas-phase reaction of SiCl$_3^+$ and H$_2$O at different levels of theory.
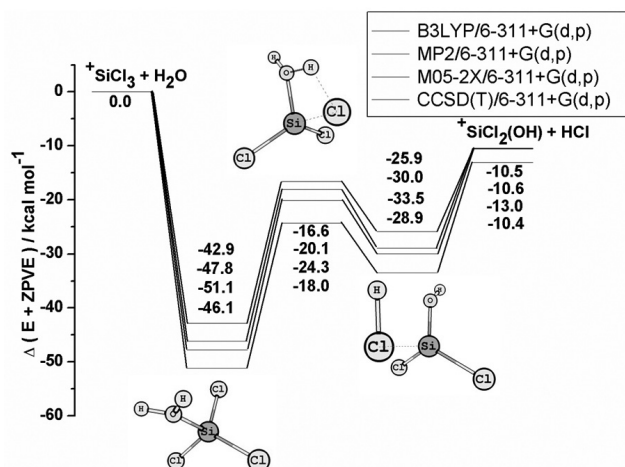

Figure 3. *Calculated energy profile for the gas-phase hydrolysis of SiCl$_3^+$ at different levels of theory*

The results of the theoretical calculations suggest that reaction 1 proceeds initially by addition of the silyl cation to the lone pair of the oxygen water. This addition is predicted to yield a strong ion-neutral binding in excess of 40 kcal mol^{-1}, and the spectrum shown in Figure 1 reveals a distinct peak corresponding the [SiCl$_3^{+\cdot}$OH$_2$] adduct corresponding to protonated trichlorosilanol. This strong binding energy is in good agreement with the experimental binding energies determined for gas-phase (CH$_3$)$_3$Si$^+$ ions with oxygen bases by high pressure mass spectrometry.[21] The large exothermicity of the association process and the low energy barrier for the system to proceed to products is responsible for the low abundance observed for the [SiCl$_3^{+\cdot}$OH$_2$] adducts. The fact that vibrational radiative emission is a relatively slow process and that collisional stabilization is inefficient at the pressures of our experiments allow us to predict that only a small fraction of the these adducts would have a sufficiently long lifetime to be observed experimentally. The calculated energy diagram also reveals that the transition state is located some 20 kcal mol^{-1} below the energy of the reactants. While the different model chemistries yield quantitative differences for the energy diagram, the qualitative profiles are similar and suggest that reaction 1 should indeed proceed rapidly.

Calculations carried for the successive hydrolysis processes (1) reveal that both the exothermicities and energy barriers for the hydrolysis of Cl$_2$SiOH$^+$ and ClSi(OH)$_2^+$ are very similar to those shown in Figure 3.

The results obtained for SiCl$_3^+$ can be compared with the fact that the corresponding CCl$_3^+$ ions are unreactive toward H$_2$O within the time scale and pressure regime typical of FT-ICR mass spectrometry.

Figure 4 displays the results of theoretical calculations performed for this system and are consistent with the slowness of the hydrolysis reaction of CCl_3^+. The main difference between the behavior of $SiCl_3^+$ and CCl_3^+ resides in the ability of the silyl cation to form a very stable adduct as shown in Figure 3. As in most gas-phase ion/molecule reactions, formation of a strongly bound ion/neutral complex is responsible for the reaction transition state to be below the energy of the reactants. In the present case, the strong association between $SiCl_3^+$ and water, as opposed to the CCl_3^+/water complex, is responsible for the transition state of the 1,3-H migration to be below the energy of the reactants.
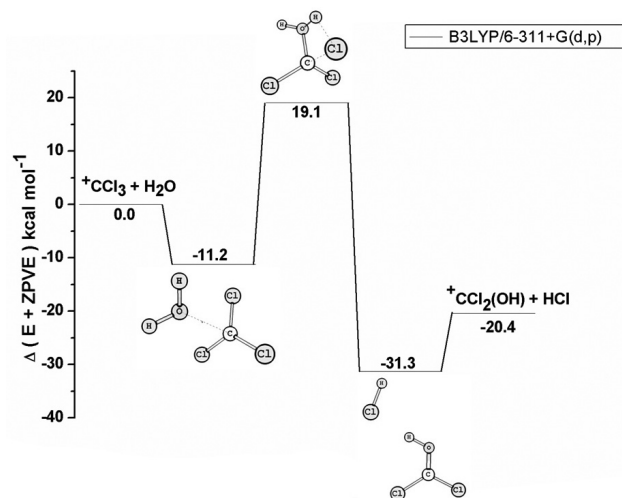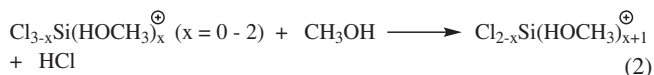

Figure 4. Calculated energy profile for the gas-phase hydrolysis of CCl_3^+ at the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory

Alcoholysis of $SiCl_3^+$

Reaction of $SiCl_3^+$ with methanol is also observed to proceed rapidly by a solvolysis-type process, reaction 2.

$$Cl_{3-x}Si(HOCH_3)_x^{\oplus} \ (x = 0 - 2) \ + \ CH_3OH \longrightarrow Cl_{2-x}Si(HOCH_3)_{x+1}^{\oplus} + \ HCl \quad (2)$$

The resulting spectrum also reveals a small fraction of CH_3^+ at *m/z* 15.

Figure 5 displays the calculated energy profile for the first methanolysis reaction and shows that formation of CH_3^+ is an endothermic process, reaction 3, and thus can only be generated by non-thermalized $SiCl_3^+$ ions.

$$\overset{\oplus}{Si}Cl_3 \ + \ CH_3OH \longrightarrow Cl_3SiOH \ + \ \overset{\oplus}{C}H_3 \quad (3)$$

The possibility of a small fraction of non-thermalized $SiCl_3^+$ ions cannot be ignored in these experiments because the methanolysis and hydrolysis occur so readily that long periods of ion cooling are not possible prior to isolation of $SiCl_3^+$ ions in the ICR cell.

Figure 5 reveals that the $[SiCl_3^+\cdots methanol]$ association, or protonated trichloromethoxysilane, is much stronger than for the water case, in agreement with the stability previously measured for the adducts of trimethylsilyl cations.[21] As a consequence of this, the energy barrier for the 1,3-H migration is further decreased and the transition for reaction 2 is calculated to be some 25 kcal mol^{-1} below the energy of the reactants.

Reaction with the higher alcohols reveals that abstraction of hydroxide with subsequent formation of a carbenium ion becomes the dominant channel and solvolysis is no longer observed. This is
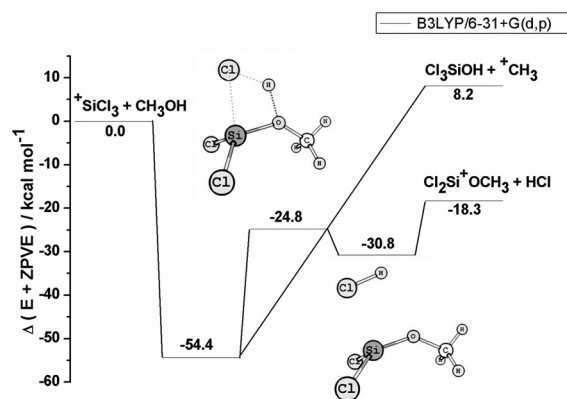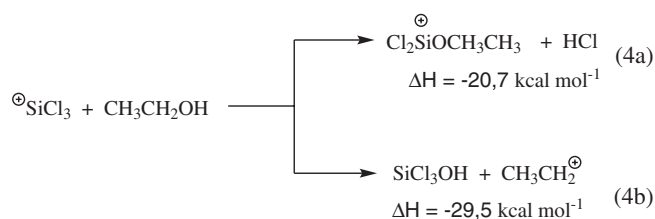

Figure 5. Calculated energy profile for the gas-phase methanolysis of $SiCl_3^+$ at the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of theory. This energy profile also considers the energetics of reaction (3) to yield CH_3^+

illustrated in Equation 4, where the formation of the carbenium ion is calculated to be the energetically preferred pathway.

$$\overset{\oplus}{Si}Cl_3 \ + \ CH_3CH_2OH \longrightarrow$$

$$Cl_2\overset{\oplus}{Si}OCH_3CH_3 \ + \ HCl \quad (4a)$$
$$\Delta H = -20{,}7 \ kcal \ mol^{-1}$$

$$SiCl_3OH \ + \ CH_3\overset{\oplus}{C}H_2 \quad (4b)$$
$$\Delta H = -29{,}5 \ kcal \ mol^{-1}$$

The experiments reveal rapid formation of $C_2H_5^+$ ions which then undergo rapid proton transfer to neutral ethanol to yield protonated ethanol, $C_2H_5OH_2^+$. Preference for carbenium ion formation becomes progressively more favorable for the higher alcohols.

Ammonolysis of $SiCl_3^+$

Gas-phase solvolysis-type reactions are also observed with ammonia, and Figure 6 shows that facile substitution occurs for the first two chlorine atoms, Equation 5.

$$Cl_{3-x}Si(NH_2)_x^{\oplus} \ (x = 0 - 1) \ + \ NH_3 \longrightarrow Cl_{2-x}Si(NH_2)_{x+1}^{\oplus} \ + \ HCl \quad (5)$$

The third substitution, leading to $Si(NH_2)_3^+$, is much slower and can only be observed at longer trapping times (trapping times > 1 s).

The calculated energy profile for the ammonolysis of $SiCl_3^+$ is shown in Figure 7 and follows a similar pattern to the previous cases discussed above. The $[Cl_3Si^+\cdots NH_3]$ adduct, protonated trichlorosilanamine, is predicted to be very stable with an stabilization energy of over 60 kcal mol^{-1}. The energy barrier for the reaction, although located well below the energy of the reactants, is calculated to be very similar to that for the hydrolysis reaction. Similar calculations for the sequential ammonolysis steps reveal that the energy barrier increases considerably. For example, the barrier for the second NH_2 substitution is calculated to be at – 14.4 kcal mol^{-1} with respect to the reactants at the MP2/6-311+G(d,p) level while the barrier for the third NH_2 substitution is calculated to be at -6.4 kcal mol^{-1} below the energy of the reactants at the MP2/6-311+G(d,p) level. This latter value is consistent with the fact that the third step in the ammonolysis reaction is much slower than the first steps.

Reaction of $SiCl_3^+$ with amines follows a similar pattern to that observed with alcohols. Solvolysis occurs readily with CH_3NH_2 but starting with $C_2H_5NH_2$ the reaction leading to initial formation of $C_2H_5^+$ becomes the preferred route over solvolysis.
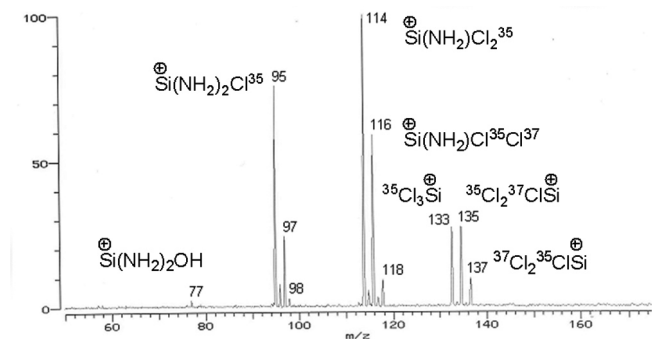
Figure 6. *Mass spectrum obtained in the FT-ICR spectrometer after 280 ms trapping time revealing the sequential ammonolysis of SiCl$_3^+$ ions. Spectrum obtained from a mixture containing nominal pressures of 2.0 x 10^{-8} Torr of SiCl$_4$ and 1.5 x 10^{-8} Torr of NH$_3$*
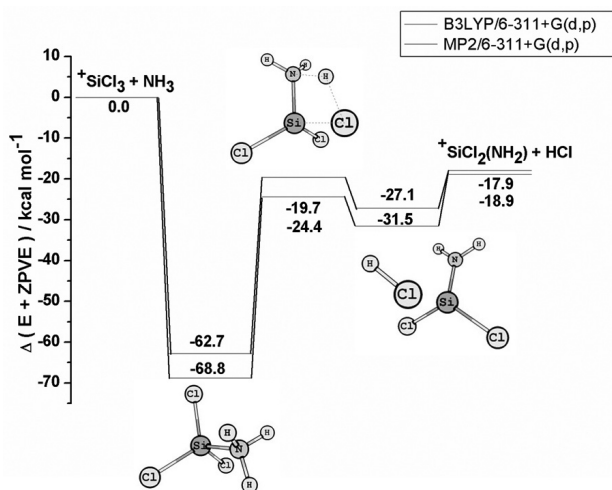

Figure 7. *Calculated energy profile for the gas-phase ammonolysis of SiCl$_3^+$ at two different levels of theory*

Reaction of SiCl$_3^+$ with other substrates

While reaction with a large number of Lewis bases could be explored, we were particularly interested in reactions with neutral substrates that would involve initial attack at a double bond center.

Preliminary experiments with propylene reveal reaction 6 to occur slowly (about 40% conversion after 5 s under our typical experimental conditions).

$$SiCl_3^+ + CH_3CH=CH_2 \longrightarrow Cl_2SiC_3H_5^+ + HCl \qquad (6)$$

Calculations of the energy profile for reaction 6 suggest that this reaction proceeds through a bridged intermediate to yield a *trans*-silyl ion as shown in Scheme 2
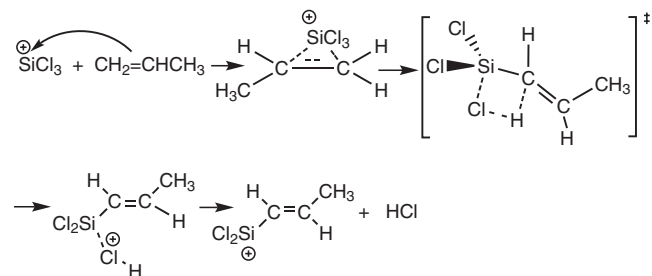
Scheme 2

CONCLUSIONS

The present work shows that gaseous SiCl$_3^+$ cations can readily undergo chlorine substitution by reaction with Lewis bases through an addition-elimination mechanism where a 1,3-H migration in the transition state results in the elimination of HCl. These reactions yield a wide variety of substituted silyl cations and provide an interesting approach for multiple substituted silyl cations. This feature is particularly interesting because it provides a convenient approach for exploring a variety of secondary condensation type ion/molecule reactions that bear strong resemblance to the fundamental reactions of sol-gel processes.[6,8]

Theoretical calculations proved to be valuable to characterize the mechanism and energetics of these reactions. For the hydrolysis of gas-phase SiCl$_3^+$ ion, DFT and *ab initio* calculations yield comparable results although some differences are observed for the energies of the transition states and intermediates of the reaction.

A comparison of the hydrolysis reaction of SiCl$_3^+$ with that of CCl$_3^+$ reveals for the first time two important differences: a) the initial adduct formation of the silyl cation with the Lewis base is much more stable than the corresponding adduct of the trichloromethyl cation; b) the energy barrier for the 1,3-H migration is considerably lower for the silyl reaction. This latter observation agrees with some previous claims that 1,3-H migration in silicon-containing ions is considerably more favorable than in carbon-containing ions.[22]

ACKNOWLEDGMENTS

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