The Protonation of Gaseous Cyclopropane

Barbara Chiavarino,[a] Maria Elisa Crestoni,[a] Andrey A. Fokin,[b] and Simonetta Fornarini*[a]

Abstract: The protonation of cyclopropane by gaseous Brønsted acids of varying strength in radiolytic experiments at atmospheric pressure leads to two distinct $C_3H_7^+$ isomers that have been sampled by their reaction with benzene. The neutral end products, $nC_3H_7{-}C_6H_5$ and $iC_3H_7{-}C_6H_5$, arise from the electrophilic aromatic substitution reaction with the $cC_3H_7^+$ and $iC_3H_7^+$ ions, respectively. Their relative abundance was studied as a function of pressure, temperature, and the presence of additives in the gaseous systems; the results indicate a large extent of isomerization to the thermodynamically favored $iC_3H_7^+$ from the protonation by strong acids. The presence of a kinetic barrier prevents any thermal isomerization from taking place in the time frame of 10^{-8} s. In the peculiar case in which protonated benzene is the Brønsted acid, $C_3H_7^+$ ions are formed in the presence of neutral benzene within the same ion–molecule complex. The ensuing reaction shows that $cC_3H_7^+$ ions are formed exclusively and react in the 10^{-10} s^{-1} estimated lifetime of the complex. Still, such $cC_3H_7^+$ ions undergo complete randomization of their hydrogen atoms; this points to a low kinetic barrier for the process. Agreement is found between the reported experimental results and updated computations of the relevant species in the $C_3H_7^+$ potential energy surface.

Keywords: gas-phase reactions · ion–molecule complexes · isomerization · proton transport · radiolysis

Introduction

Among $C_3H_7^+$ species, three possible isomers have received major consideration in both experimental and theoretical studies, $iC_3H_7^+$, $cC_3H_7^+$, and $nC_3H_7^+$. The $iC_3H_7^+$ cation is recognized as the most stable isomer.[1] As the conjugate acid of propene, its heat of formation is of fundamental importance in gas-phase thermochemistry. Its value has been recently redetermined as 808 kJ mol^{-1} (298 K) by a high-resolution photoelectron photoion coincidence method.[2] The ion $iC_3H_7^+$ is also the simplest all-carbon and hydrogen carbenium ion to be prepared as a stable species in superacid media,[3] in which it was found to undergo scrambling of both hydrogen and carbon atoms.[4, 5] The key intermediates and/or transition structures for these processes were suggested to be $nC_3H_7^+$ and $cC_3H_7^+$.[4] The $cC_3H_7^+$ ion itself has been identified as a discrete species in the gas-phase in which propene and cyclopropane are characterized by nearly the same proton affinity (PA).[6] As cyclopropane is 29 kJ mol^{-1} higher in energy with respect to propene, it is inferred that $cC_3H_7^+$ is less stable than $iC_3H_7^+$ by the same energy difference. $cC_3H_7^+$ is therefore prone to isomerize to $iC_3H_7^+$, namely the thermodynamically favoured species. Indeed, whereas the lifetime of gaseous $cC_3H_7^+$ ions is estimated to exceed 10^{-7} s, an isomerization to $iC_3H_7^+$ has been suggested to account for the identical collisional activation spectra of the ions obtained by the protonation of cyclopropane and propene after a time lapse of about 10^{-5} s.[6c] $cC_3H_7^+$ ions have been proposed to play a role in various ionic processes in the gas phase. For example, it has been suggested as the intermediate in the CH_3^+ reaction with ethylene[7] and it has been conceived as the possible product ion of the hydrogen atom loss from ionized propane.[8] The metastable dissociation of propane molecules from cluster ions of $C_3H_7^+$ with neat propane or Ar/propane has also been ascribed to the isomerization of a $cC_3H_7^+$ core to give $iC_3H_7^+$ proceeding by way of a transient $nC_3H_7^+$.[9] The difference between the heats of formation of $nC_3H_7^+$ and $iC_3H_7^+$ has been determined as 87 kJ mol^{-1} according to photoelectron spectroscopy data, though all attempts to trap $nC_3H_7^+$ have shown that it rearranges in less than 10^{-10} s.[6b, 10]

The present paper describes an experimental study on the protonation of cyclopropane by gaseous Brønsted acids of different acid strength, aimed to assess the significant factors affecting the formation of $cC_3H_7^+$ and its isomerization into $iC_3H_7^+$. The experiments have been performed at pressures

---

[a] Prof. S. Fornarini, Dr. B. Chiavarino, Dr. M. E. Crestoni
Dipartimento di Studi di Chimica e Tecnologia
delle Sostanze Biologicamente Attive
Università di Roma "La Sapienza", P.le A. Moro 5
00185 Roma (Italy)
Fax: (39) 06-4991-3602
E-mail: simonetta.fornarini@uniroma1.it

[b] Prof. A. A. Fokin
Department of Organic Chemistry
Kiev Polytechnic Institute
37 Pobeda Ave., 03056, Kiev (Ukraine)

0947-6539/01/0713-2916 $ 17.50+.50/0

close to one atmosphere, under conditions ensuring efficient collisional thermalization of excited intermediates, and by using the radiolytic method for the generation of ions.[11] The ionic species of interest, $c\mathrm{C_3H_7^+}$ and $i\mathrm{C_3H_7^+}$, were trapped by reaction with benzene. The ensuing products of electrophilic aromatic substitution, $n\mathrm{C_3H_7{-}C_6H_5}$ and $i\mathrm{C_3H_7{-}C_6H_5}$, provide a dependable probe of the relative amounts of $c\mathrm{C_3H_7^+}$ and $i\mathrm{C_3H_7^+}$, respectively, that are present in the ionic medium.[12] Their formation is ascribed to the sequence of steps that characterize the electrophilic aromatic substitution by gaseous cations [Eqs. (1) and (2)].[11, 13]

$$c\mathrm{C_3H_7^+} + \mathrm{C_6H_6} \rightarrow n\mathrm{C_3H_7{-}C_6H_6^+} \xrightarrow[-\mathrm{BH^+}]{+\mathrm{B}} n\mathrm{C_3H_7{-}C_6H_6} \tag{1}$$

$$i\mathrm{C_3H_7^+} + \mathrm{C_6H_6} \rightarrow i\mathrm{C_3H_7{-}C_6H_6^+} \xrightarrow[-\mathrm{BH^+}]{+\mathrm{B}} i\mathrm{C_3H_7{-}C_6H_6} \tag{2}$$

The ionic electrophile and the aromatic substrate react within a collision complex to form an intermediate arenium ion which yields the neutral substitution product upon deprotonation by a base (B). An alternative mechanism for the electrophilic aromatic substitution reaction in the gas phase has been recently reported, in which the reaction is promoted by the protonated aromatic compound.[14] For example, the reaction of toluenium ions with propene leads to neutral cymene by a stepwise mechanism involving a proton transfer within the $[\mathrm{MeC_6H_6^+ \cdot C_3H_6}]$ collision complex yielding the $[\mathrm{MeC_6H_5} \cdot i\mathrm{C_3H_7^+}]$ ion–molecule complex, whereby the aromatic alkylation of toluene by the so-formed isopropyl cation takes place [Eq. (3)]. This route has been exploited to provide an alternative protonating agent of $c\mathrm{C_3H_6}$, in our case protonated benzene, $\mathrm{C_6H_7^+}$, which yields the reactive nucleophile in the same event of proton transfer and, most important, within the same collision complex.

$$\begin{aligned} &\mathrm{Me{-}C_6H_6^+} + \mathrm{C_3H_6} \rightarrow [\mathrm{Me{-}C_6H_6^+ \cdot C_3H_6}] \rightarrow [\mathrm{Me{-}C_6H_5} \cdot i\mathrm{C_3H_7^+}] \\ &\qquad \rightarrow [i\mathrm{C_3H_7{-}C_6H_5{-}Me^+}] \xrightarrow[-\mathrm{BH^+}]{+\mathrm{B}} i\mathrm{C_3H_7{-}C_6H_4{-}Me} \end{aligned} \tag{3}$$

The experimental investigation has been combined with theoretical calculations. $\mathrm{C_3H_7^+}$ ions have long been a benchmark problem of computational studies,[15] converging to common agreement on the higher stability of $i\mathrm{C_3H_7^+}$ with respect to $c\mathrm{C_3H_7^+}$, whereas $n\mathrm{C_3H_7^+}$ does not lie in a local minimum. In the present study CCSD(T) results are presented on the three $\mathrm{C_3H_7^+}$ isomers of interest and on the transition states connecting them.

Experimental Section

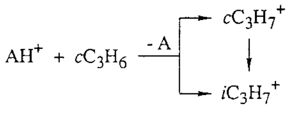
Materials: Research grade gases (> 99.9 mol% pure) were purchased from Matheson Gas Products or Fluka, with the exception of MeF (99 mol% pure) which was obtained from Fluorochem. ^{13}C-depleted benzene was obtained from Isotec, with an isotopic purity of 99.9% ^{12}C atoms. All chemicals used as reagents or as reference standards for the characterization of products and MS fragmentation patterns in GLC-MS analyses were purchased from commercial sources or prepared according to conventional procedures.

Radiolytic experiments: Gaseous samples have been prepared in sealed Pyrex vessels according to described procedures.[11, 13] Irradiations were performed at 30 °C in a 220 Gammacell (Nuclear Canada) for two hours at the dose rate of 10^4 Gy h^{-1}. The radiolytic products were extracted by freezing the vessel in liquid nitrogen and introducing *n*-hexane. The cold walls of the vessel were carefully washed, and the solution was analyzed by GLC-MS with a Hewlett–Packard 5890 gas chromatograph equipped with a Model 5989B quadrupole mass spectrometer. The analyses were performed in triplicate by using a 50 m long, 0.32 mm inner diameter, fused silica capillary column (PONA column from Hewlett–Packard) operated in the temperature range from 40 °C to 160 °C. The radiolytic products of interest were identified by comparison of their retention times and mass spectra with those of authentic samples. When labeling experiments were performed the site of deuterium incorporation into the products, for example, the alkyl group versus the aromatic ring in *n*-propylbenzene and isopropylbenzene, was determined from the relative abundance of labeled and unlabeled fragment ions of diagnostic value, for example, those deriving from ethyl and methyl group loss from the molecular ion of *n*-propylbenzene and isopropylbenzene, respectively. In order to verify that no isotope scrambling takes place in the fragmentation process, appropriately labeled specimen compounds were synthesized and their mass spectra were checked.

Computational details: All computations were carried out with the Gaussian 98 v.5 program package.[16] The geometries optimized at MP2(full)/6–311G** level were characterized by harmonic frequency analysis to ascertain the nature of the stationary points (NIMAG = 0 for minima and 1 for transition structures). Zero-point vibrational energies (ZPVEs), were scaled[17] by factor 0.95. Reaction pathways along both directions from the transition structures were followed by the IRC method.[18] Taking the obtained MP2(full)/6–311G** structures as the starting point, all geometries have been reoptimized at coupled cluster[19] CCSD(T)[20] method with Dunning's correlation-consistent polarized double-zeta (cc-pVDZ) basis set.[21] To refine the final relative energies, the CCSD(T)/cc-pVDZ geometries were further subjected to single-point CCSD(T)/cc-pVTZ calculations; our final energies are at CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ + ZPVE(MP2(full)/6–311G**) level.

Results and Discussion

Direct protonation of cyclopropane: The results of the radiolytic experiments, namely the pattern of the neutral products obtained from the reaction of the ionic intermediates with benzene, are collected in Table 1. The ionic species of interest in this study are the ones formed by protonation of cyclopropane by a Brønsted acid, which derives from the interaction of ionizing radiation with a bulk gas at atmospheric pressure according to well-established sequences of events.[11] The Brønsted acids ($\mathrm{H_3^+}$ or $\mathrm{D_3^+}$ in bulk $\mathrm{H_2}$ or $\mathrm{D_2}$, $\mathrm{CH_5^+}$ and $\mathrm{C_2H_5^+}$ in bulk $\mathrm{CH_4}$, $\mathrm{C_2H_5^+}$ in bulk $\mathrm{C_2H_6}$), the primary ionic reagents in the gaseous mixture, undergo collisional quenching of any excess energy content, which may derive from their formation processes, by thermalizing collisions with the unreactive bulk gas. Ultimately, they react with the basic additives, cyclopropane, benzene, or other added neutral species, in a statistical ratio, given the typically high exothermicity of the process. The thermochemical parameters of the significant proton transfer processes (Table 2) are derived from the relative PA values of the neutral species undergoing proton exchange; these are obtained from the same database.[22] The first entries of Table 1 characterize systems in which unlabelled reagent ions, ordered with their increasing acid strength, deliver their proton chiefly to cyclopropane [Eq. (4)], the additive present in major concentration.



$$\mathrm{AH^+} + c\mathrm{C_3H_6} \xrightarrow{-\mathrm{A}} \left\{ \begin{array}{l} c\mathrm{C_3H_7^+} \\ \quad\downarrow \\ i\mathrm{C_3H_7^+} \end{array} \right. \tag{4}$$

Table 1. Radiolytic alkylation of benzene by cC_3H_6 under activation by gaseous Brønsted acids.

System composition [Torr][a]			Reagent	Products[b]			
C_6H_6	bulk gas	additives	ion		isopropylbenzene [%]	n-propylbenzene [%]	CF/FC [%/%]
1.4[c]	C_2H_6 (560)		$C_2H_5^+$		10	90	[d]
0.4	CH_4 (100)		$CH_5^+/C_2H_5^+$		59	41	[d]
0.4[c]	CH_4 (560)		$CH_5^+/C_2H_5^+$		56	44	[d]
0.4	CH_4 (560)		$CH_5^+/C_2H_5^+$		57	43	[d]
1.0[c]	CH_4 (585)		$CH_5^+/C_2H_5^+$		56	44	[d]
2.8[c]	CH_4 (590)		$CH_5^+/C_2H_5^+$		58	42	[d]
0.75	H_2 (545)	CO (20)	HCO^+		61	39	[d]
0.75	H_2 (560)	CO (20)/Et_3N (0.25)	HCO^+		63	37	[d]
0.75[e]	D_2 (570)	Et_3N (0.3)	D_3^+	CF	0	100	13
				FC	73	27	87
1.05[e]	D_2 (545)	CO (20)	DCO^+	CF	0	100	12
		Et_3N (0.25)		FC	73	27	88
1.2[e,f]	D_2 (530)	CO (20)	DCO^+	CF	0	100	9
		Et_3N (0.25)		FC	75	25	91
1.0[e]	D_2 (570)	SO_2 (20)	DSO_2^+	CF	0	100	10
		cyclohexanone (0.25)		FC	84	16	90
0.7[e]	D_2 (570)	Et_3N (0.31)	$C_3H_3F_3OD^+$	CF	0	100	5
		CH_3COCF_3 (25)		FC	85	15	95

[a] All systems contained cC_3H_6 (2 Torr) and O_2 (15 Torr), as radical scavenger, unless stated otherwise. [b] The product pattern is illustrated according to the isomer distribution deriving from the direct protonation and mediated protonation pathways (FC and CF, respectively) whose relative contribution (%) is given in the third column. [c] cC_3H_6 (10 Torr). [d] Not available. [e] ^{13}C-depleted benzene was used. [f] Experiment run at 120 °C instead of usual 30 °C.

Table 2. Experimental proton affinities of relevant neutral species (A).[a]

A	PA [kJ mol^{-1}]
cyclopropane	749
propene	751
H_2	422
CO	594
CH_4	543
C_2H_4	680
SO_2	672
CH_3COCF_3	723
C_6H_6	749
$CH_3C_6H_5$	783
$CF_3C_6H_5$	702[b]

[a] Ref. [22], unless stated otherwise. [b] Ref. [23].

The ensuing ions, $cC_3H_7^+$ and $iC_3H_7^+$, sampled by reaction with benzene [Eqs. (1) and (2)], are found in different ratios, the relative amount of $iC_3H_7^+$ being rather high when the protonation is effected in CH_4, from which a relatively strong acid, CH_5^+, is formed together with $C_2H_5^+$. A similarly high yield of iC_3H_7–C_6H_5 with respect to nC_3H_7–C_6H_5 was reported from the D_3^+ reaction under comparable conditions.[12] However, when $C_2H_5^+$, a milder Brønsted acid, is the only reagent ion only a minor fraction of iC_3H_7–C_6H_5 is formed. The question arises as to the mechanism and the timing of the $cC_3H_7^+$ to $iC_3H_7^+$ isomerization, since any isomerization at the stage of the intermediate arenium ions, converting nC_3H_7–$C_6H_6^+$ into iC_3H_7–$C_6H_6^+$, has been disproven.[12] To this end the influence of factors known to affect ionic reactions in the gas phase was checked in the methane systems. It may first be conceived that a highly exothermic protonation process, releasing a certain amount of excess energy in the $cC_3H_7^+$ ion so formed, may allow its subsequent isomerization to $iC_3H_7^+$. The isomerization of excited $cC_3H_7^+$ is expected to compete with its thermalization by photon emission or by unreactive collisions with the bulk gas, the latter being by far the prevailing process at atmospheric pressure.[24] Decreasing the pressure to 100 Torr lowers frequency of thermalizing collisions and should result in a higher fraction of $iC_3H_7^+$. In contrast with this expectation the iC_3H_7–C_6H_5 versus nC_3H_7–C_6H_5 distribution stays approximately constant and also appears insensitive to changes in the concentration of benzene. Benzene is the nucleophile that incercepts both cations [Eqs. (1) and (2)] and, thus, its concentration affects the lifetime of these ions in the medium which can be estimated on the order of 10^{-8} s. The observed invariance indicates that possibly excited $cC_3H_7^+$ ions do not isomerize in the 10^{-10} s time frame (the time lapse between collisions with CH_4 at 300 Torr) and that thermal $cC_3H_7^+$ ions do not isomerize in 10^{-8} s (the time for a reactive collision with benzene at 2 Torr).[25] These results are clear evidence of a sizeable barrier preventing the $cC_3H_7^+ \rightarrow iC_3H_7^+$ isomerization.

Mediated protonation of cyclopropane: Not until recently was an alternative mechanism found to lead to aromatic alkylation products from an ionic sequence of reactions initiated by the collision of a protonated aromatic compound with a proelectrophile, as described in Equation (3). In the present study the active proelectrophile is cyclopropane and this so-called Crafts–Friedel pathway (CF)[14] is verified by the use of labelled reagents.

Labeled Brønsted acids are obtained either in neat D_2 (D_3^+) or in the presence of D_2 and 20–25 Torr of additives such as CO, CF_3COCH_3, and SO_2, in which DCO^+, $CF_3C(CH_3)OD^+$, and DSO_2^+, respectively, are formed by D^+ transfer from D_3^+. The labeled Brønsted acid (AD^+) delivers a deuteron to benzene to form a benzenium ion, whereby fast equilibration of the seven H/D atoms is attained before the encounter with a cyclopropane molecule.[26] Within the collision complex a statistically favored H^+ transfer forms $C_3H_6D^+$ ions, which are trapped by the neutral benzene within the lifetime of the ion–molecule complex [Eqs. (5a) and (5b)].

$$AD^+ + C_6H_6 \rightarrow A + C_6H_6D^+ \tag{5a}$$

$$\begin{aligned} C_6H_6D^+ + cC_3H_6 &\rightarrow [C_6H_6D^+ \cdot cC_3H_6] \rightarrow [C_6H_6D \cdot C_3H_7^+] \\ &\rightarrow [C_3H_7\text{–}C_6H_6D^+] \xrightarrow[-BH^+]{+B} C_3H_7\text{–}C_6H_4D \end{aligned} \tag{5b}$$

The occurrence of multistep processes within ion–molecule complexes, including proton transfer events, is well documented in gas-phase ion chemistry in which they play a mechanistically relevant role.[27] Finally, in a statistically weighed majority of events, the neutral alkylation product is characterized by the presence of a D atom on the aromatic ring at variance with the direct mechanism of aromatic substitution by an already formed cationic electrophile, in which the D atom is expected to be on the alkyl group [so-called Friedel–Crafts pathway (FC), Eqs. (6a) and (6b)].

$$AD^+ + cC_3H_6 \rightarrow A + C_3H_6D^+ \tag{6a}$$

$$\begin{aligned} C_3H_6D^+ + C_6H_6 &\rightarrow [C_3H_6D^+ \cdot C_6H_6] \\ &\rightarrow [C_3H_6D{-}C_6H_6^+] \xrightarrow[-BH^+]{+B} C_3H_6D{-}C_6H_5 \end{aligned} \tag{6b}$$

The presence of a base (Et_3N typically, except in the experiments run with SO_2, since this compound is known to give Lewis adducts with gaseous Et_3N)[28] ensures fast deprotonation of the intermediate arenium ions, which may otherwise undergo H/D exchange with active neutral species in the radiolytic medium.[29] Mass spectral analysis of the alkylation products identifies the site of deuteration. The isomeric propylbenzenes can therefore be assigned to either mechanism with the results shown in the second part of Table 1. Notably, the CF pathway leads to the exclusive formation of $nC_3H_7{-}C_6H_5$, suggesting $cC_3H_7^+$ as the only ionic intermediate. This result is consistent both on the grounds of the nearly thermoneutral proton transfer between protonated benzene and cyclopropane (Table 2) and of the prompt nucleophilic trapping of the $cC_3H_7^+$ ion by the same benzene molecule within the ion–molecule complex, a process estimated to occur in a timescale of about 10^{-10} s.[14e] The formation of the CF product is inhibited as the proton transfer from the arenium ion to cyclopropane becomes endothermic. Such a case occurred in the attempt to react toluenium ions ($Me{-}C_6H_6^+$) formed from the methylation of benzene by Me_2F^+. The CF products are instead favored when the PA of arene becomes lower. A significant yield of CF alkylation products is thus obtained from the reaction of protonated α,α,α-trifluorotoluene ($CF_3{-}C_6H_6^+$) formed by the reaction of benzene with CF_3^+ ions from the radiolysis of CF_4. As shown in Equations (7a) and (7b), the isomer formed is still the *n*-propyl derivative in spite of an exothermicity of 47 kJ mol^{-1} for the proton transfer reaction (Table 2). The reaction of the deuterated arenium ion, formed as shown in Equations (7a) and (7b), implies a deuteron transfer to cyclopropane within the complex ending with a D atom in the side chain.

$$CF_3^+ + C_6D_6 \rightarrow CF_3C_6D_6^+ \tag{7a}$$

$$\begin{aligned} CF_3C_6D_6 + cC_3H_6 &\rightarrow [CF_3C_6D_6^+ \cdot cC_3H_6] \rightarrow [CF_3C_6D_5 \cdot cC_3H_6D^+] \\ &\rightarrow [nC_3H_6D{-}C_6D_5CF_3^+] \xrightarrow[-BH^+]{+B} nC_3H_6D{-}C_6D_4CF_3 \end{aligned} \tag{7b}$$

The determination of the site of deuteration in the side chain, that is, $C_2H_5{-}CHD{-}C_6D_4CF_3$ 30% and $C_2H_4D{-}CH_2{-}C_6D_4CF_3$ 70%, is consistent with a statistical distribution of D in the *n*-propyl group of $nC_3H_6D{-}C_6D_4CF_3$. This finding provides a strong indication that fast equilibration of hydrogen atoms has occurred in the $cC_3H_6D^+$ ion within the $[CF_3C_6D_5 \cdot cC_3H_6D^+]$ complex. At the same time it disproves an alternative possibility of concerted D^+ transfer and C–C bond formation, which is expected to lead to $DCH_2CH_2CH_2{-}C_6D_4CF_3$ as the only product.

Given the typically 2:1 ratio between the concentration of cyclopropane and benzene in the experiments with labeled Brønsted acids, it is noteworthy that the CF pathway contributes only to a minor extent to the overall substitution products (last column in Table 1). It is reasonable to infer that in those experiments in which the ratio is even higher, as in the methane experiments, this contribution will be negligible, thus accounting for the observed invariance of the $nC_3H_7{-}C_6H_5$ versus $iC_3H_7{-}C_6H_5$ product ratio with respect to changes in the concentration of benzene. Any contribution of the CF pathway would in fact increase the relative amount of $nC_3H_7{-}C_6H_5$, a result more likely to appear at the highest benzene concentration; however, this fails to produce any significant change in the product distribution.

The use of labeled Brønsted acids yields information on the FC product pattern as well. In fact, the isomer distribution of the FC pathway shows that the yield of the isomerization product isopropylbenzene is highest from the reaction of $CF_3C(CH_3)OD^+$ and DSO_2^+ in spite of a lower exothermicity of the D^+ transfer to cyclopropane with respect, for example, to DCO^+. There is clearly an effect caused by the chemical features of the D^+ donor itself. The finding that such weaker Brønsted acids do in fact yield substantial amounts of $iC_3H_7^+$ may be ascribed to the detailed mechanism of proton transfer within the collision complex, $[AH^+ \cdot cC_3H_6] \rightarrow [A \cdot iC_3H_7^+]$, in which A, a polar molecule, may catalyze the $cC_3H_7^+ \rightarrow iC_3H_7^+$ process, probably facilitating the required H migration. Polar neutral species are in fact known to catalyze the isomerization of species that require a proton to be carried from one site to another, a process that is favored when the neutral species has a PA value intermediate between those of the two sites.[30] Alternatively, the presence of a polar molecule (A) may affect the relative stability of isomeric $C_3H_7^+$ ions within $[A \cdot C_3H_7^+]$ complexes.[31, 32]

Finally, neither the CF nor the FC pathway are sensitive to a temperature change from the usual 30 °C up to 120 °C. It appears then that even bare $cC_3H_7^+$ ions do not undergo any thermal isomerization process in the observation time window of 10^{-8} s. Assuming a pre-exponential factor of ca. 10^{13} this result implies the existence of an activation barrier in excess of 38 kJ mol^{-1} for the $cC_3H_7^+ \rightarrow iC_3H_7^+$ isomerization. At the same time the experiments in C_2H_6 suggest that the protonation by $C_2H_5^+$, which is exothermic by 69 kJ mol^{-1}, may still be effective in yielding $iC_3H_7^+$ ions, so that the range experimentally found for this activation barrier appears to be comprised between 38 and 69 kJ mol^{-1}.

The computed $C_3H_7^+$ isomers and their interconversion pathways: As shown in Figure 1, which summarizes the computed structures and relative energies at CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ + ZPVE(MP2(full)/6–311G**) level, the protonation of cyclopropane yields an unsymmetrical corner-protonated MIN1 as the most stable isomer retaining the three-membered ring. The edge-protonated

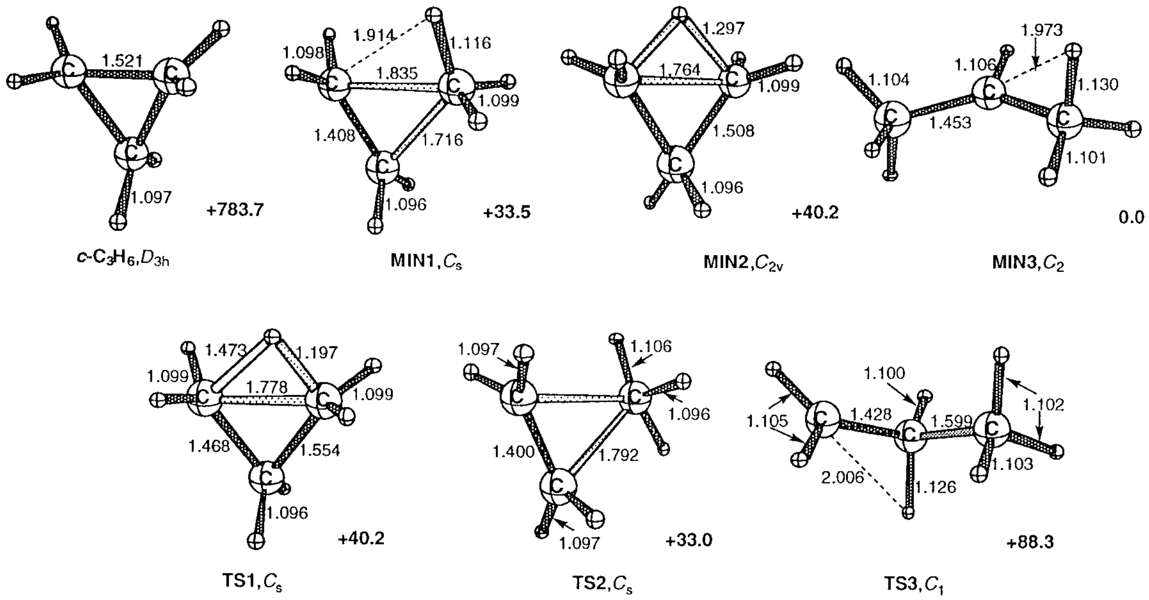


Figure 1. The CCSD(T)/cc-pVDZ optimized geometries and relative CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ + ZPVE(MP2(full)/6–311G**) energies (kJ mol^{-1}) for cyclopropane and some important $C_3H_7^+$ species. Bond lengths are in Å.

isomer MIN2 is 7 kJ mol^{-1} less stable The barrier for MIN1 rearrangement to MIN2 via TS1 is 7 kJ mol^{-1}. The rotation of the methyl group within MIN1 via a symmetrical corner-protonated TS2 is virtually free. The investigated portion of the $C_3H_7^+$ potential energy surface (PES) shows that hydrogen scrambling should be a fast process occurring through a 1,2-H shift by way of edge-protonated MIN2, accompanied by a barrierless methyl rotation in corner-protonated MIN1. The global minimum on the $C_3H_7^+$ PES, corresponding to the $iC_3H_7^+$ ion (MIN3) is also taken as the reference energy level in reporting the relative energies of the various species (Table 3). The process which is of major interest in this work, the one regarding the $cC_3H_7^+ \rightarrow iC_3H_7^+$ reaction, is found to take place in a synchronous way by C–C bond fission in concert with H migration and rotation of the terminal methylene group, as shown in TS3. The activation energy for the process, 55 kJ mol^{-1} (i.e., from MIN1 to MIN3 via TS3), is within the range estimated from the gathered experimental evidence.

Table 3. Total energies, zero-point vibrational energies (ZPVE), and relative energies (including ZPVE corrections) for cC_3H_6 and $C_3H_7^+$ isomers.

Species	Total energy[a] [hartree]	ZPVE[b] (NIMAG)[c] [kJ mol^{-1}]	Relative energy [kJ mol^{-1}]
cC_3H_6	– 117.66924	206.5 (0)	783.7
MIN1 (corner)$cC_3H_7^+$	– 117.96432	231.1 (0)	33.5
MIN2 (edge)$cC_3H_7^+$	– 117.96155	230.7 (0)	40.2
MIN3 $iC_3H_7^+$	– 117.97312	223.2 (0)	0.0
TS1	– 117.96141	229.9 (1)	40.2
TS2	– 117.96417	230.3 (1)	33.0
TS3	– 117.94139	225.7 (1)	88.3

[a] CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ. [b] Scaled by factor 0.95. [c] Number of imaginary vibrational modes.

The reported theoretical results fit into the general description of the $C_3H_7^+$ species provided by recent computational approaches. In particular, the relative energies of the (corner) and (edge)$cC_3H_7^+$ are within less than 4 kJ mol^{-1} from the corresponding values obtained at MP4(fc)/6–311G**//MP2(full)/6–311G** level of theory.[15b,c] The agreement with data obtained by density functional methods is less satisfactory as these calculations predict (corner) and (edge)-$cC_3H_7^+$ to be relatively higher in energy by 13–33 kJ mol^{-1}.[15d]

Conclusion

This study has addressed the protonation of cC_3H_6 in the gas phase, the possibility to form different isomers, and their interconversion pathways. The protonation has been effected either directly, by the primary Brønsted acids formed by known ionic reaction sequences in the bulk component of the gaseous mixture, or indirectly, by an intermediate proton transfer step to some additive. The ensuing ionic species, $cC_3H_7^+$ and $iC_3H_7^+$, have been sampled by reaction with benzene. This additive itself may be protonated and act as a Brønsted acid towards cC_3H_6. In such a case, the situation arises that the conjugate base, the benzene molecule formed in the proton transfer event, may also act as the trapping nucleophile operating in the so-called Crafts–Friedel mode. In the radiolytic experiments performed at pressures close to one atmosphere, the two isomers are found in comparable amounts and the isomerization of $cC_3H_7^+$ into the thermodynamically favored isomer $iC_3H_7^+$ is never complete. The experimental product pattern has shown that whereas the effect of bulk parameters that typically affect ion–molecule reactions in the gas phase, such as temperature and pressure, is negligible, at least within the range investigated, the features of the ion–molecule pair that react within the collision complex are most important. The invariance of the product ratio with pressure suggests that the $cC_3H_7^+$ versus $iC_3H_7^+$ ratio is decided at the time of the proton transfer event rather than due to a subsequent isomerization of any excited

$cC_3H_7^+$ ions. Strong Brønsted acids, such as D_3^+ or CH_5^+, favor the conversion into the isomerized product $iC_3H_7^+$, whose formation from bare $cC_3H_7^+$ requires a substantial activation energy. The estimated range of this barrier, 38–69 kJ mol^{-1}, is in good agreement with the theoretical evaluation of 55 kJ mol^{-1}. The nearly thermoneutral proton transfer from $C_6H_7^+$ yields exclusively $cC_3H_7^+$, which is trapped by benzene within the same ion–molecule complex in the CF pathway. The same mechanism accounts for the formation of $nC_3H_6D{-}C_6D_4CF_3$ from the reaction of $CF_3C_6D_6^+$ with cC_3H_6. The complete H scrambing in protonated cyclopropane within the intermediate complex $[CF_3C_6D_5 \cdot cC_3H_6D^+]$ is consistent with the fast rate expected for this process and speaks in favor of a discrete $cC_3H_6D^+$ ion existing within the complex. The H randomization is bound to occur within the lifetime of such complexes estimated to be on the order of 10^{-10} s^{-1}, in agreement, once again, with the low activation barrier predicted by the theoretical calculations.

Acknowledgements

The authors acknowledge the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica and the Consiglio Nazionale delle Ricerche for financial support and are grateful to Professor Fulvio Cacace for helpful discussions.

---

[1] a) P. Vogel, *Carbocation Chemistry*, Elsevier, Amsterdam, **1985**; b) G. K. S. Prakash, P. von R. Schleyer, *Stable Carbocation Chemistry*, Wiley, New York, **1997**.

[2] T. Baer, Y. Song, C. Y. Ng, J. Liu, W. Chen, *J. Phys. Chem. A* **2000**, *104*, 1959.

[3] G. A. Olah, G. K. S. Prakash, J. Sommer, *Superacids*, Wiley, New York, **1985**.

[4] M. Saunders, P. Vogel, E. L. Hagen, J. Rosenfeld, *Acc. Chem. Res.* **1973**, *6*, 53.

[5] M. Saunders, A. P. Hewett, O. Kronja, *Croat. Chem. Acta* **1992**, *65*, 673.

[6] a) S.-L. Ching, J. L. Franklin, *J. Am. Chem. Soc.* **1972**, *94*, 6347; b) D. J. McAdoo, F. W. McLafferty, P. F. Bente, *J. Am. Chem. Soc.* **1972**, *94*, 2027; c) P. P. Dymerski, R. M. Prinstein, P. F. Bente, F. W. McLafferty, *J. Am. Chem. Soc.* **1976**, *98*, 6834; d) F. Cacace, A. Guarino, M. Speranza, *J. Am. Chem. Soc.* **1971**, *93*, 1088.

[7] R. N. Abernathy, F. W. Lampe, *Int. J. Mass Spectrom. Ion Phys.* **1981**, *41*, 7.

[8] D. J. McAdoo, S. Olivella, A. Solé, *J. Phys. Chem. A* **1998**, *102*, 10798.

[9] M. Foltin, Z. Herman, T. D. Märk, *Int. J. Mass Spectrom. Ion Processes.* **1995**, *149/150*, 415.

[10] a) S. G. Lias, R. E. Rebbert, P. Ausloos, *J. Am. Chem. Soc.* **1970**, *92*, 6430; b) J. C. Schultz, F. A. Houle, J. L. Beauchamp, *J. Am. Chem. Soc.* **1984**, *106*, 3917.

[11] a) F. Cacace, *Acc. Chem. Res.* **1988**, *21*, 215; b) F. Cacace, in *Structure/Reactivity and Thermochemistry of Ions* (Eds.: P. Ausloos, S. G. Lias), Reidel, Dordrecht, **1987**; c) F. Cacace, in *Organic Reactivity: Physical and Biological Aspects* (Eds.: B. T. Golding, R. J. Griffin, H. Maskill), The Royal Society of Chemistry, London, **1995**.

[12] M. Attinà, F. Cacace, P. Giacomello, *J. Am. Chem. Soc.* **1980**, *102*, 4768.

[13] a) S. Fornarini, M. E. Crestoni, *Acc. Chem. Res.* **1998**, *31*, 827; b) S. Fornarini, *Mass Spectrom. Rev.* **1996**, *15*, 365.

[14] a) M. Aschi, M. Attinà, F. Cacace, *Angew. Chem.* **1995**, *107*, 1719; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1589; b) M. Aschi, M. Attinà, F. Cacace, *J. Am. Chem. Soc.* **1995**, *117*, 12832; c) M. Aschi, M. Attinà, F. Cacace, *Res. Chem. Intermed.* **1996**, *22*, 645; d) M. Aschi, F. Cacace, A. Troiani, *Angew. Chem.* **1997**, *107*, 116; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 83; e) M. Aschi, M. Attinà, F. Cacace, G. D'Arcangelo, *J. Am. Chem. Soc.* **1998**, *120*, 3982; f) M. Aschi, M. Attinà, F. Cacace, *Chem. Eur. J.* **1998**, *4*, 1535; g) F. Cacace, B. Chiavarino, M. E. Crestoni, *Chem. Eur. J.* **2000**, *6*, 2024.

[15] a) K. Raghavachari, R. A. Whiteside, J. A. Pople, P. von R. Schleyer, *J. Am. Chem. Soc.* **1981**, *103*, 5649; b) W. Koch, B. Liu, P. von R. Schleyer, *J. Am. Chem. Soc.* **1989**, *111*, 3479; c) W. Koch, P. von R. Schleyer, P. Buzek, B. Liu, *Croat. Chem. Acta* **1992**, *65*, 655; d) M. V. Frash, V. B. Kazansky, A. M. Rigby, R. A. van Santen, *J. Phys. Chem. B* **1997**, *101*, 5346; e) M. J. S. Dewar, E. A. Healy, J. M. Ruiz, *J. Chem. Soc. Chem. Commun.* **1987**, 943; f) W. Klopper, W. Kutzelnigg, *J. Phys. Chem.* **1990**, *94*, 5625.

[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.5*, Gaussian, Pittsburgh PA, 1998.

[17] A. T. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.

[18] C. Gonzales, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

[19] a) M. Urban, J. Noga, S. J. Cole, R. J. Bartlett, *J. Chem. Phys.* **1985**, *83*, 4041; b) R. J. Bartlett, J. D. Watts, S. A. Kucharski, J. Noga, *Chem. Phys. Lett.* **1990**, *165*, 513. c) "Coupled-Cluster Theory": J. Gauss in *Encyclopedia of Computational Chemistry* (Eds.: P. von R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, H. F. Schaefer III, P. R. Schreiner), Wiley, Chichester, **1998**, pp. 615–636.

[20] P. J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* **1993**, *98*, 5219.

[21] D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358.

[22] E. P. Hunter, S. G. Lias, *NIST Chemistry Webbook, NIST Standard Reference Database Number 69*, (Eds.: W. G. Mallard, P. J. Linstrom), National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov), **2000**.

[23] M. Aschi, B. Chiavarino, M. E. Crestoni, S. Fornarini, *J. Phys. Chem.* **1996**, *100*, 19859.

[24] a) R. C. Dunbar, *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 423; b) R. C. Dunbar, *Mass Spectrom. Rev.* **1992**, *11*, 309.

[25] a) M. T. Bowers, T. Su, in *Interactions between Ions and Molecules* (Ed.: P. Ausloos), Plenum, New York, **1975**; b) T. Su, M. T. Bowers, in *Gas Phase Ion Chemistry* (Ed.: M. T. Bowers), Academic Press, New York, **1979**.

[26] a) C. H. DePuy, R. Gareyev, S. Fornarini, *Int. J. Mass Spectrom. Ion Processes* **1997**, *161*, 43; b) B. Chiavarino, M. E. Crestoni, S. Fornarini, C. H. DePuy, R. Gareyev, *J. Phys. Chem.* **1996**, *100*, 16201; c) D. Kuck, *Mass Spectrom. Rev.* **1990**, *9*, 583.

[27] a) R. D. Bowen, *Acc. Chem. Res.* **1991**, *24*, 364; b) D. J. McAdoo, T. H. Morton, *Acc. Chem. Res.* **1993**, *26*, 295; C. Matthias, D. Kuck, *Org. Mass Spectrom.* **1993**, *28*, 1073; D. Berthomieu, V. Brenner, G. Ohanessian, J. P. Denhez, P. Millié, H. E. Audier, *J. Am. Chem. Soc.* **1993**, *115*, 2505; H.-F. Grützmacher, *Int. J. Mass Spectrom. Ion Processes* **1992**, *118/119*, 825.

[28] K. R. Leopold, M. Canagaratna, J. A. Phillips, *Acc. Chem. Res.* **1997**, *30*, 57.

[29] B. Chiavarino, M. E. Crestoni, B. Di Rienzo, S. Fornarini, *J. Am. Chem. Soc.* **1998**, *120*, 10856.

[30] a) D. K. Bohme, *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95; b) J. W. Gauld, L. Radom, *J. Am. Chem. Soc.* **1997**, *119*, 9831.

[31] P. von R. Schleyer, K. Laidig, K. B. Wiberg, M. Saunders, M. Schindler, *J. Am. Chem. Soc.* **1988**, *110*, 300.

[32] D. Farcasiu, D. Hancu, *J. Am. Chem. Soc.* **1999**, *121*, 7173.

Received: November 24, 2000 [F2897]