205. The Gas-Phase Ion/Molecule Reactions of C_3H_5X ($X = Cl, Br, I$)

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(22.X.90)

The ion/molecule reactions of the molecular ion, the $C_3H_5^+$ ion, and the $C_3H_3^+$ ion obtained from 3-chloropropene, 1-bromopropene, 2-bromopropene, 3-bromopropene, bromocyclopropane, and 3-iodopropene have been studied with their neutral precursor in a *Fourier*-transform mass spectrometer (FT/ICR). The molecular ions react to yield primarily $C_6H_9^+$ except for the ion derived from 1-bromopropene that is unreactive. The kinetics of the 3-bromopropene molecular ion reveals that 18% of these ions must possess a different structure which is unreactive. The fact that $C_3H_5^+$ ions obtained from 2-bromopropene are the only ones to undergo proton transfer is taken as evidence that only this parent compound gives rise to 2-propenyl cations by low-energy electron impact. The $C_3H_3^+$ ions generated in these systems are shown to be roughly an equal mixture of propargylium ions that react to yield $C_6H_7^+$ and unreactive cyclopropenium ions.

Introduction. – Gas-phase ion/molecule reactions and self chemical ionization can often provide a powerful approach towards the identification of isomeric compounds. In addition, these experiments can also become a selective tool in the recognition of different ionic structures, as these reactions are usually carried out under very mild conditions and near thermal equilibrium. A relevant example, among many, that is directly linked to our present work, is the early study by ICR of the ion chemistry of monofluoropropenes [1]. The outcome of the low-energy ion/molecule reactions in these compounds was instrumental in showing that, while the different isomers display nearly identical mass spectra, the corresponding molecular ions, $C_3H_5F^{+\cdot}$, exhibit very distinct reactivity.

A preliminary acount of the ion/molecule reactions of other related 3-halopropene systems, $CH_2{=}CHCH_2X$ ($X = Cl, Br, I$), has revealed that the chemistry is very unlike the fluoro derivative [2]. This is obvious, since the $C_3H_5^+$ ion, a minor fragment upon ionization of C_3H_5F, becomes the base peak in the mass spectra of the systems mentioned above. Both the fragment ion and the molecular ions have been shown to react in a very similar fashion. While the reactivity of the allyl cation has been explored in a variety of cases [3] [4], the reactivity pattern in the halopropenes remains an area of potential interest, because they are prone to undergo reactions, which can be explained on the basis of a mechanism consistent with gas-phase cycloaddition reactions [5][6].

The fact that the molecular ions of the above mentioned halopropenes react in an allyl-cation fashion has prompted us to carry out a more thorough investigation of the ion/molecule chemistry of several isomeric halopropenes. The study of these reactions is also timely, because they bear some insight on the lively discussion regarding the structure of the $C_3H_5^+$ ions generated from different C_3H_5X parent compounds by electron impact. The molecular ions, $C_3H_5Br^{+\cdot}$, derived from bromocyclopropane and the 1-bromo-, 2-bromo-, and 3-bromopropenes have been shown to retain their isomeric identity based on their IR multiphoton-dissociation spectra [7]. In the meantime, collision-induced experiments of $C_3H_5^+$ ions generated from 3-bromopropene indicate these to be allyl cations [8–10]. Some controversy remains as to whether fragmentation at higher electron energies [9] or at higher accelerating voltages in a collision-activated dissociation (CAD) experiment may give rise to other isomeric structures. By contrast, the $C_3H_5^+$ ions generated from 2-bromopropene have been regarded as corresponding to the 2-propenyl cation based on the same type of experiments. Nevertheless, the CAD data with ^{13}C-labelled ions suggest that some rearrangement must take place, *at least* prior to dissociation [11] [12]. For both of these cases, the $C_3H_5^+$ ions are produced with very small average kinetic-energy releases in the metastable transitions indicating a straightforward bond-breaking process [8]. The situation is more complex in bromocyclopropane, where the $C_3H_5^+$ ions are produced with a higher kinetic-energy release, and for which the CAD spectra favor an allyl structure and cast some doubt on a stable cyclic structure. The 1-bromopropene also gives rise to $C_3H_5^+$ ions with higher kinetic-energy release [8], and the CAD spectra is consistent with a large fraction of species having an allyl-cation structure. No evidence of a stable 1-propenyl cation could be observed. Yet, the CAD evidence relies on small differences in fragmentation such that caution is necessary for conclusive statements.

The present report covers the study of the ion/molecule reactions in neat 3-chloropropene, 1-bromopropene, 2-bromopropene, 3-bromopropene, bromocyclopropane, and 3-iodopropene to provide some further evidence on the nature of the $C_3H_5^+$ ions involved in the different cases. In addition, the reactive behavior of the molecular ions suggests that some of the isomers may be better represented by a structure that closely resembles that of the $C_3H_5^+$ ions. The main reactions of the $C_3H_5^+$ fragment originating from the different bromo compounds was briefly described by *Lay* and *Gross* [4], and an attempt was made to establish the structure of the ions from their reaction with benzene followed by collisional dissociation of the adduct. Our work extends some of the early findings with particular emphasis on the molecular-ion reactivity.

Experimental. – Ion/molecule reactions were investigated in a *Fourier*-transform ICR spectrometer operating at a constant magnetic field of 1.4 T and controlled by a *Nicolet FTMS-1000* data system. Typical experiments were carried out at pressures in the range of 5 to 7.5×10^{-8} mbar (ionization gauge reading).

Kinetic experiments were conducted by ejection of all primary ions except for the ion of interest with a pulse tailored by the SWIFT excitation technique [13]. The FT experiments were carried out in the broadband mode, and intensities were checked against the known composition of Xe isotopes. Most of the experiments used ionization energies in the range of 12 to 14 eV (filament to trap) except for experiments designed to verify the ionization-energy dependence of the formation of isomeric ions.

Rate constants k were calculated by fitting the time decay of the normalized reactant ion intensity to a proper exponential function through a simplex optimization procedure [14]. Absolute rate constants were estimated by calibrating the ion gauge for the well known ion/molecule rate constant of the methane molecular ion, and correcting the pressure by the estimated polarizability of the halopropenes. While the trends for the reported rate constants are reproducible and reliable among the series, the accuracy of the absolute values is hard to determine, and is probably no better than 30%. The branching ratios reflecting relative rate constants are assumed to be accurate to better than 10%.

Experiments with 3-bromopropene were also carried out in a *Spectrospin* FT spectrometer operating at 4.7 T without ejection of any primary ions. Observation of the peaks at m/z 81 and m/z 79 under very high-resolution conditions reveals these to be a single peak corresponding to the $C_6H_9^+$ and $C_6H_7^+$ species, respectively.

Samples of 3-chloropropene, 1-bromopropene, 2-bromopropene, bromocyclopropane, 3-bromopropene, and 3-iodopropene were either distilled or purified by GC.

Results and Discussion. – The mass spectra of 3-chloropropene, 1-bromopropene, 2-bromopropene, 3-bromopropene, bromocyclopropane, and 3-iodopropene display three major primary ions: $C_3H_3^+$ (*m/z* 39), $C_3H_5^+$ (*m/z* 41), and the molecular ion $M^{+\cdot}$. The first fragment ion becomes negligible at the lower electron energies used to study the kinetics of the ion/molecule processes.

Table 1. *Product Distribution, Percentage of Reactive Ions, and Rate Constant for the Reaction of $C_3H_3^+$ Ions with Their Neutral Precursors*

	$C_3H_5^+$	$C_6H_5^+$	$C_6H_7^+$	%[a]	k[b]
1-Bromopropene	0.20	0.26	0.54	36	28
2-Bromopropene	0.38	0.24	0.38	34	24
Bromocyclopropane	0.60	0.06	0.34	41	15
3-Bromopropene	0.66	–	0.34	53	14

[a] This column refers to the percentage of reactive ions, presumably corresponding to the $HCCCH_2^+$ ion.

[b] Rate constants in units of 10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.

Table 1 lists the product distribution for the reactions of $C_3H_3^+$ in the bromopropenes under conditions, where tertiary reactions from $C_3H_5^+$ are still negligible. The main reactions are

$$C_3H_3^+ + C_3H_5Br \rightarrow C_3H_5^+ + C_3H_3Br \quad (1)$$

$$\rightarrow C_6H_7^+ + HBr \quad (2)$$

The depletion of $C_3H_3^+$ ions is very fast, but reaches a large non-zero constant value. This suggests the presence of a large fraction of unreactive ions. This observation is in agreement with our earlier results [2], and presumably reflects reaction of the $HCCCH_2^+$ species and inertness of the cyclopropenium ion as suggested in [15]. The fraction of reactive species has been found to be unusually insensitive to ionization energy. Furthermore, the ratio of propargylium ion/cyclopropenium ion is mildly dependent on the parent compound. Yet, there are sizeable differences in rate constants and in product distribution. This latter variation may reflect differences in the structures, and, therefore, stabilities, of the product $C_3H_5^+$ ions.

Table 2. *Product Distribution and Rate Constant for the Reaction of $C_3H_5^+$ Ions with Their Neutral Precursors*

	$C_6H_9^+$	$C_6H_7^+$	$C_4H_7^+$	Other	
	products	k[a]			
3-Chloropropene	0.35	0.32	0.13	$C_4H_7^+$ $C_3H_4Cl^+$ $C_4H_6Cl^+$	15
1-Bromopropene	0.48	0.39	0.13		15
2-Bromopropene	0.25	0.21	–	$(C_3H_5Br)H^+$ 0.54	11
Bromocyclopropane		0.24	0.61	0.15	6
3-Bromopropene	0.52	0.41	0.07	–	16
3-Iodopropene	0.55	0.45	–	–	22

[a] Rate constants in units of 10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.

Table 2 lists the product distribution for the reactions of the $C_3H_5^+$ ions with their precursors. Two main reactions are observed in all cases except for the species derived from 2-bromopropene which undergoes preferential proton transfer.

$$C_3H_5^+ + C_3H_5Br \rightarrow C_6H_9^+ + HBr \tag{3}$$

$$\rightarrow C_6H_7^+ + HBr + H_2 \tag{4}$$

Observation of the proton transfer reaction by the $C_3H_5^+$ ions derived from $CH_2{=}C(Br)CH_3$ clearly indicates the 2-propenyl structure for this ion. It is well known that the $CH_2{=}C^+{-}CH_3$ ions can readily transfer a proton to a species with higher proton affinity, whereas the $(CH_2CHCH_2)^+$ ion does not undergo facile proton transfer [16]. The above finding is further confirmed by an experiment in which, after ion selection in the 2-bromopropene case, C_3H_5I is introduced through a pulsed valve resulting in the formation of $(C_3H_5I)H^+$. Since the products associated with a cycloaddition-type mechanism (*Reactions 3* and *4*) are also observed to contribute appreciably, it is not possible to conclude, whether the 2-propenyl ion also undergoes this type of reaction, or some contribution from the allylic form is responsible for this observation. However, the isomerization of the 2-propenyl species to the more stable allyl cation has been calculated to involve a relatively high barrier of 71 kJ/mol [17]. The kinetic analysis of the $C_3H_5^+$ derived from 2-bromopropene yields no evidence of a double exponential decay, a behavior that could be difficult to detect, if the rate constants for the two species are very similar.

The data from *Table 2* favors the idea that the $C_3H_5^+$ ions originating from 1-bromopropene must be at least 90%, or more, allylic (or some other form that undergoes slow proton transfer), as no evidence of protonated products could be detected. While the proton affinity of the different C_3H_5Br isomers is not known, the known trends for related compounds suggest that they will be higher than that of allene and methylacetylene [18]. Thus, these observations reflect the nature of the $C_3H_5^+$ ions rather than differences of the neutrals.

It is also noticeable that, except for bromocyclopropane, the branching ratio for $C_6H_9^+$ and $C_6H_7^+$ is remarkably alike. This strongly suggests that very similar mechanisms are operative for all these reactions. It is reasonable to assume that the $C_6H_7^+$ ions originate from energetic $C_6H_9^+$ species:

$$C_3H_5^+ + C_3H_5X \rightarrow (C_6H_{10}X^+)^* \rightarrow C_6H_9^+ + HX \tag{5}$$

$$(C_6H_{10}X^+)^* \rightarrow C_6H_7^+ + H_2 + HX \tag{6}$$

The ion $C_6H_9^+$ is unreactive towards further chemistry with the substrates used in this work. While both experimental evidence [19] and theoretical calculations at the semi-empirical [19] [20] and *ab-initio* level [20] predict the 1-methylcyclopentenylium ion to be the most stable species, there is no data at present to establish the identity of such a species. In earlier experiments [21], $C_6H_7^+$ was observed to be consistent with a protonated benzene structure, as the product of *Reaction 4* readily transfers a proton to C_2H_5OH but very slowly to CH_3OH.

While it seems logical to assume that the initial $[C_6H_{10}X]^+$ complex probably involves a halonium ion prior to rearrangement and subsequent H shift, the large partition into

$C_6H_7^+$ for the bromocyclopropane reaction probably reflects the much higher exothermicity expected for *Reaction 3* for the case of the cyclic compound.

A minor product, not reported in the earlier work [2] [4], corresponding to $C_4H_7^+$, is likely to be the methylallyl cation, as it undergoes fast reaction with the substrates to yield an ion $C_7H_{11}{}^+$, identified as the product of a process similar to *Reaction 2*.

While the reactions observed for $C_3H_5^+$ in our work are consistent with the previous MS evidence, they argue against the formation of the 2-propenyl form from 1-bromopropene. The elusive question regarding the stability of the 1-propenyl and cyclopropyl cation remains an open problem raised by the early calculations [22], but predicted by the more recent and extensive *ab-initio* results [17].

Table 3. *Product Distribution and Rate Constant for the Reaction of the Molecular Ions with Their Neutral Precursors*

	$C_6H_{10}X^+$	$C_6H_9^+$	Other products		k[a])
3-Chloropropene	–	0.43	0.09	$C_4H_7^+$ $C_5H_7^+$ 0.39	0.7
1-Bromopropene		unreactive			
2-Bromopropene	0.30	0.70	–	–	6.2
Bromocyclopropane	0.48	0.28	0.19	$C_4H_7^+$	0.6
3-Bromopropene	–	1	–	–	8[b])
3-Iodopropene	0.06	0.88	0.06	–	9.8

[a]) Rate constants in units of 10^{-10} cm^3·molecule^{-1}·s^{-1}.

[b]) Refers to the reactive molecular ion species.

Finally, *Table 3* lists the product distribution for the molecular ions of the different precursors. Some observations are particularly important in this case: *a*) the molecular ion of the 1-bromopropene is unreactive within the time scale of the ICR experiment; *b*) the 3-chloropropene molecular ion reacts with its precursor very slowly, and it may approach a large constant non-zero value which could not be determined very accurately given the slowness of the reaction. The corresponding reaction for the 3-bromopropene is unusually interesting, because it clearly levels out at (18 ± 2)% of the initial amount of

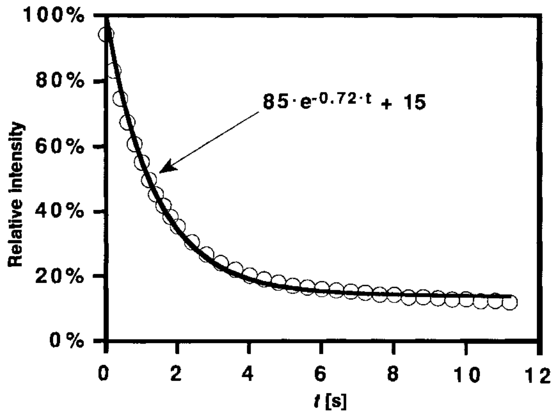

Figure. *A typical plot of the normalized intensity of the molecular ion of 3-bromopropene* (sum of the two isotopic species) *as a function of reaction time showing the approach to a constant non-zero value* the molecular ion (*Fig.*). This behavior has been identified as being due to different isomeric species [23]. This fraction of unreactive ions has been found to be independent of ionization energy and pressure. By comparison, the molecular ion of 3-iodopropene reacts to completion.

The ease with which the molecular ions of the 3-halopropenes react in a fashion similar to the corresponding $C_3H_5^+$ ion,

$$C_3H_5Br^{+\cdot} + C_3H_5Br \rightarrow C_6H_9^+ + HBr + Br\cdot \qquad (7)$$

suggests that, for the Br and I case, the molecular ion may have a structure which resembles more closely that of an ion/neutral complex, $C_3H_5^+ (X\cdot)$. This view is supported by the small energy for dissociation of the Br and I species [24].

$$CH_2{=}CHCH_2Br^{+\cdot} \rightarrow C_3H_5^+ + Br\cdot \qquad \Delta H_{298} = 39.5\ \mathrm{kJ/mol} \qquad (8)$$

$$CH_2{=}CHCH_2I^{+\cdot} \rightarrow C_3H_5^+ + I\cdot \qquad \Delta H_{298} = 55.8\ \mathrm{kJ/mol} \qquad (9)$$

Preliminary calculations [25] using the semi-empirical AM1 method [26] show that the most stable structure for the molecular ion of 3-bromopropene and 3-iodopropene corresponds to a species where the C—halogen bond length has been elongated to a value considerably beyond its normal bond length and close to a symmetric position between C(1) and C(3). The same calculations place this structure for the 3-chloropropene above the energy of the normal molecular ion. More refined calculations are presently under way to explore this idea, since experiments using IR multiphoton dissociation of the above cations argue against the identification of the unreactive ionic species being simply the result of rearrangement to a 1-bromopropene molecular ion [23].

The slow rate constant observed for the bromocyclopropane cation and the lack of reactivity of the 1-bromopropene cation fit very well with the notion of a reverse activation energy for the formation of $C_3H_5^+$ obtained from the metastable-peak analysis [8]. Yet, the large amount of $C_6H_{10}Br^+$ observed in bromocyclopropane is intriguing and may reflect a different type of initial ion/neutral complex requiring more energy to undergo further rearrangements. The same product in 2-bromopropene is somewhat more difficult to explain. Yet, it is noticeable that the 2-bromopropene molecular ion does not promote any proton transfer, thus, suggesting that this molecular ion may not be easily represented by the model used for the 3-halopropenes. Unfortunately, there is no thermochemical data available to make estimates of the energies involved for such processes.

The results outlined in this work point out that the most stable structure for of the molecular ions of 3-bromopropene and 3-iodopropene may differ considerably from their neutral counterpart. On the other hand, with exception of the 1-bromopropene molecular ion which is unreactive, the different molecular ions $C_3H_5Br^{+\cdot}$ exhibit similar chemistry, unlike the case of the fluoropropenes, but with very distinct branching ratios.

The authors acknowledge the support of the *Swiss National Science Foundation*, the *Federal Commission for the Encouragement of Research*, and *Spectrospin*, Fällanden. We would also like to thank the support of the *Sao Paulo Science Foundation, FAPESP*, the *BID-USP* program and the *Brazilian Research Council, CNPq*. We also thank *S. Haebel* for help with operation of the *Spectrospin* spectrometer and *A. Heusler* for preparation of the samples.

REFERENCES

[1] C.J. Drewery, G.C. Goode, K.R. Jennings, *Int. J. Mass Spectrom. Ion Phys.* **1976,** *20,* 403.

[2] J.M. Riveros, S.E. Galembeck, *Int. J. Mass. Spectrom. Ion Phys.* **1983,** *47,* 183.

[3] M.W.E.M. v. Tilborg, R.v. Doorn, N.M.M. Nibbering, *Org. Mass. Spectrom.* **1980,** *15,* 152.

[4] J.O. Lay, Jr., M.L. Gross, *J. Am. Chem. Soc.* **1983,** *105,* 3445.

[5] D.H. Russell, M.L. Gross, in 'Lectures Notes in Chemistry. Ion Cyclotron Resonance Spectrometry', Ed. H. Hartmann, K.-P. Wanczek, 1978, Vol. 7, pp. 209–231.

[6] C. Dass, M.L. Gross, *J. Am. Chem. Soc.* **1984,** *106,* 5775; G.S. Groenewold, M.L. Gross, *ibid.* **1984,** *106,* 6559; *ibid.* **1984,** *106,* 6575.

[7] T. Gäumann, J.M. Riveros, Z. Zhu, *Helv. Chim. Acta* **1990,** *73,* 1215.

[8] R.D. Bowen, D.H. Williams, H. Schwarz, C. Wesdemiotis, *J. Am. Chem. Soc.* **1979,** *101,* 4681.

[9] M.T. Bowers, L. Shuying, P. Kemper, R. Stradling, H. Webb, D.H. Aue, J.R. Gilbert, K.R. Jennings, *J. Am. Chem. Soc.* **1990,** *102,* 4832.

[10] P.C. Burgers, J.L. Holmes, A.M. Mommers, J.E. Szulejko, *Org. Mass. Spectrom.* **1983,** *18,* 596.

[11] N. kieu My, M. Schilling, H. Schwarz, *Org. Mass Spectrom.* **1987,** *22,* 113.

[12] N. kieu My, M. Schilling, H. Schwarz, *Org. Mass. Spectrom.* **1987,** *22,* 254.

[13] A.G. Marshall, T.-C. Lin Wang, T.L. Ricca, *J. Am. Chem. Soc.* **1985,** *107,* 7893.

[14] P.C. Jurs, 'Computer Software Applications in Chemistry', John Wiley and Sons, Inc., New York, 1986, Chapt. 9.

[15] P.J. Ausloos, S.G. Lias, *J. Am. Chem. Soc.* **1981,** *103,* 6505.

[16] D.H. Aue, W.R. Davidson, M.T. Bowers, *J. Am. Chem. Soc.* **1976,** *98,* 6700.

[17] K. Raghavachari, R.A. Whiteside, J.A. Pople, P.v.R. Schleyer, *J. Am. Chem. Soc.* **1981,** *103,* 5649.

[18] D.H. Aue, M.T. Bowers, in 'Gas Phase Ion Chemistry', Ed. M.T. Bowers, Academic Press, New York, 1979, Vol. II, pp. 1–52.

[19] T. Gäumann, R. Houriet, D. Stahl, J.C. Tabet, N. Heinrich, H. Schwarz, *Org. Mass Spectrom.* **1983,** *18,* 215.

[20] S.E. Galembeck, Doctoral Thesis, University of São Paulo, São Paulo, Brazil, 1988.

[21] J.M. Riveros, S.E. Galembeck, unpublished results.

[22] L.C. Radom, P.C. Hariharan, J.A. Pople, P.v.R. Schleyer, *J. Am. Chem. Soc.* **1973,** *95,* 6531.

[23] T. Gäumann, Z. Zhu, M.C. Kida, J.M. Riveros, submitted for publication.

[24] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, *J. Phys. Chem. Ref. Data* **1988,** *17,* Suppl. 1.

[25] P. Carrupt, J.M. Riveros, D. Stahl, private communication.

[26] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.P.P. Stewart, *J. Am. Chem. Soc.* **1985,** *107,* 3902.