Reactions of He^3H^+ Ions with Gaseous Hydrocarbons. IV. Cyclobutane, Cyclopentane, and Cyclohexane

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Abstract: Gaseous carbonium ions were produced from the protonation of cyclobutane, cyclopentane, and cyclohexane with helium tritide molecular ions, obtained from the β decay of molecular tritium. A fraction of the excited carbonium ions formed from the exothermic protonation are collision stabilized at pressures ranging from 100 to 400 Torr, and yield in all systems stabilized cycloalkanium ions. The latter can partially rearrange to the isomeric linear carbonium ions. The results obtained provide direct evidence for the existence of the gaseous cyclobutanium, cyclopentanium, and cyclohexanium ions.

We have recently reported on the gas-phase protonation of toluene,[1] methane and ethane,[2] and cyclopropane, propane, isobutane, and *n*-butane[3] with an extremely strong acid, the helium tritide molecular ion, which is formed in the β decay of molecular tritium.

The major findings of these studies, carried out under conditions excluding the interference of radiolytic processes, were that the He^3H^+ ions react either as a Brønsted acid, protonating the organic substrate

$$He^3H^+ + RH \longrightarrow RH^3H^+ + He \qquad (1)$$

or undergo a hydride ion transfer

$$He^3H^+ + RH \longrightarrow R^+ + H-{}^3H + He \qquad (2)$$

The first reaction mode leads to the formation of labeled carbonium ions, and eventually of labeled neutral products, which can be separated and determined by radio gas chromatography.

The second reaction mode yields only one tritiated product, namely hydrogen tritide, which also can be approximately determined by low-temperature gas–solid chromatography.

The possibility of actually isolating the final, neutral products, to determine their structure and the position of the tritium atom within their molecule, represents a distinct advantage in the study of the gaseous carbonium ions, since it provides a clue to the structure of the protonated hydrocarbon that cannot be established by a purely mass spectrometric technique.

In the present study, we have extended the investigation to the next lower cycloalkanes, from cyclobutane to cyclohexane, since the determination of the structure of the protonated cycloparaffins appears of particular interest, in view of the isomerism of these ions with the corresponding protonated olefins, and with the $C_nH_{2n+1}^+$ ions from the fragmentations of the alkanes.

Experimental Section

Materials. The cyclopentane and cyclohexane employed for the preparation of the samples and for the determination of the retention volumes in the radio gas chromatographic analyses were Research Grade products from Fluka A.G. Their purity, checked by vpc, was found to exceed 99.9 mole %. The cyclobutane was prepared from cyclobutanone, according to the procedure described by Roberts.[4] The purity of the product was checked by ir spectrometry, as well as by vpc. Methane, ethane, and the other gaseous hydrocarbons used for identification purposes were research grade samples from Soc. Rivoira (Turin, Italy). The 1-hexene, *trans*-2-hexene, *cis*-2-hexene, 3-hexene, 1-pentene, and *trans*-2-pentene were Fluka A.G. Research Grade chemicals. The radio gas chromatographic analysis of tritium gas, obtained from Commissariat a l'Energie Atomique (France) with a stated purity of over 95%, revealed the presence of two impurities, hydrogen tritide and tritiated methane, whose activity accounted respectively for 0.35 and 0.10% of the molecular tritium activity. The basic technique employed in the present work involves the production of He^3H^+ ions from the decay of a tracer amount of molecular tritium, diluted in a large excess of the organic substrate, at a pressure of a few hundreds Torr.

Full details on the procedure for the preparation, the storage, and the analysis of the samples were given in the previous papers of this series.[1-3]

The following vpc columns were employed for the separation and the determination of the tritiated reaction products. A 6-m column packed with ethylene glycol saturated with silver nitrate on Celite C 22, operated at room temperature, was used for the separation of the isomeric C_4–C_6 olefins. A 12-m dimethylsulfolane on Celite C 22 column, operated at room temperature, or a 2-m didecyl phthalate on Celite C 22 column, was used for the separation of the C_4–C_6 cycloalkanes and the lower alkanes. Finally, the gaseous products were analyzed with a 6-m silica gel column at 100°.

Results and Discussion

Cyclobutane. The yields of the tritiated products formed from the protonation of cyclobutane with He^3H^+ ions at 400 Torr are shown in Table I. The major products isolated were tritiated *trans*-2-butene, ethylene, propylene, and cyclobutane, whose yields were unaffected when the experiments were carried out in the absence of added oxygen.

The first step in the formation of the labeled products is the protonation of cyclobutane by the He^3H^+ ions, according to the equation

$$He^3H^+ + c\text{-}C_4H_8 \longrightarrow (C_4H_9{}^*)^+_{exc} + He \qquad (3)$$

where the asterisk indicates, as in the following equations, a species containing a tritium atom.

Reactions analogous to process 3 were observed by mass spectrometric techniques using other protonating agents, namely CH_5^+, H_3^+, or D_3^+, and organic substrates such as the lower alkanes,[5-7] cyclopropane,[8] and a number of cyclopentanes and cyclohexanes.[9]

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(1) F. Cacace and S. Caronna, *J. Am. Chem. Soc.*, **89**, 6848 (1967).
(2) F. Cacace, R. Cipollini, and G. Ciranni, *ibid.*, **90**, 1122 (1968).
(3) F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *ibid.*, **90**, 2222 (1968).
(4) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).
(5) V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 2307 (1966).
(6) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965).
(7) F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in

Table I. Yields of the Products from the Reactions of He^3H^+ Ions with Cyclobutane + 2% O_2 at 400 Torr

Tritiated product	Yield,[a] %
Methane	1.3[b] ± 0.1
Ethane	6.1 ± 0.2
Ethylene	11.1 ± 0.7
Propylene	8.4 ± 0.8
trans-2-Butene	12.1 ± 0.4
Cyclobutane	6.9 ± 0.1
Total yield of organic tritiated products	45.9%

[a] The yield given in the table represents the percentual fraction of the tritium activity originally contained in the He^3H^+ decay ions which is found in each product. [b] Each yield is the mean value of at least four different analyses, carried out on two different stored samples.

As to the protonation of the cyclobutane itself, a reaction similar to process 3 was reported in 1965 by Ausloos and Lias,[10] who used D_3^+ ions formed in the radiolysis of D_2–cyclobutane mixtures.

While the enthalpy change associated with process 3 cannot be precisely calculated, owing to the lack of information on the heat of formation of protonated cyclobutane, there is no doubt that the protonation is strongly exothermic. The excited carbonium ion from reaction 3 can either undergo collisional stabilization at a pressure of 400 Torr, or decompose into simpler ions.

$$(C_4H_9{}^*)^+{}_{exc} + M \longrightarrow C_4H_9{}^{*+} + M_{exc} \qquad (4)$$

The observed $C_4H_8{}^*$ tritiated hydrocarbons, isolated as neutral, final products, are likely to arise from the thermoneutral proton-transfer process involving a stabilized protonated ion and a molecule of cyclobutane.

$$C_4H_9{}^{*+} + c\text{-}C_4H_8 \longrightarrow C_4H_9{}^+ + C_4H_8{}^* \left\{\begin{array}{c}\text{cyclobutane}\\ + \\ trans\text{-2-butene}\end{array}\right. \qquad (5)$$

Similar fast, thermoneutral proton-transfer process have been frequently observed, for instance, from protonated methane, ethane, propane, cyclopropane, isobutane, toluene, etc., to the corresponding hydrocarbons.[1–3,5]

Owing to the large excess of the inactive cyclobutane contained in the system, reaction 5 causes the whole activity originally contained in the stabilized protonated ions to be transferred into the $C_4H_8{}^*$ tritiated hydrocarbons, whose combined yield (cyclobutane 6.9% + *trans*-2-butene 12.1%) indicates that about 20% of the excited ions from reaction 3 are collision stabilized in cyclobutane at 400 Torr.

The isolation of tritiated cyclobutane seems difficult to explain without the assumption that at least part of the $C_4H_9{}^{*+}$ carbonium ions retain a cyclic structure, and we therefore regard the present results as direct evidence in favor of the existence of the cyclobutanium ion. The formation of tritiated *trans*-2-butene indicates, on the other hand, that a large fraction of the stabilized protonated cyclobutane rearranges to a linear structure, probably corresponding to a secondary butyl ion

$$c\text{-}C_4H_9{}^{*+} \longrightarrow sec\text{-}C_4H_9{}^{*+} \qquad (6)$$

which is eventually converted to the *trans*-2-butene through reaction 5. It should be noted, in this connection, that Ausloos and Lias, who protonated $c\text{-}C_4H_8$ with radiolytically formed H_3^+ ions, in the presence of $c\text{-}C_6D_{12}$, isolated only $CH_3CH_2CHDCH_3$ as the final deuterated product, and concluded that the protonated cyclobutane rearranges to a *sec*-butyl ion structure.

Such discrepancy with the present results can be easily explained, if one takes into account, on one hand, the large extent of the isomerization to a linear structure observed even in our experiments, carried out in pure cyclobutane at the pressure of 400 Torr, and, on the other hand, the large excess of hydrogen (ratio H_2:$c\text{-}C_4H_8 = 600$) used by Ausloos and Lias. There is little doubt that, under their conditions, the large number of collisions with the inert H_2 molecules was largely sufficient to allow the complete isomerization of the cyclic $C_4H_9{}^+$ ions to the *sec*-butyl ion structure.[11]

It is also of interest to note that, among the possible linear butenes, only the most stable *trans*-2-butene was actually isolated in the present study.

The other tritiated products observed arise from the fragmentation of the excited carbonium ions formed in reaction 3, either directly, as the tritiated methane and ethylene

$$(C_4H_9{}^*)^+{}_{exc} \longrightarrow CH_4{}^* + C_3H_5{}^{*+} \qquad (7)$$

$$(C_4H_9{}^*)^+{}_{exc} \longrightarrow C_2H_4{}^* + C_2H_5{}^{*+} \qquad (8)$$

or from the exothermic hydride ion transfer from cyclobutane to the C_3 fragment ions

$$C_3H_5{}^{*+} + c\text{-}C_4H_8 \longrightarrow C_3H_6{}^* + C_4H_7{}^+ \qquad (9)$$

$$C_2H_5{}^{*+} + c\text{-}C_4H_8 \longrightarrow C_2H_6{}^* + C_4H_7{}^+ \qquad (10)$$

Processes similar to reactions 9 and 10 have been observed by Doepker and Ausloos[12] in the gas phase radiolysis of cyclobutane.

Cyclopentane. The yields of the tritiated products from the protonation of cyclopentane with He^3H^+ ions at 100 Torr are summarized in Table II. The major product formed is tritiated cyclopentane, with smaller yields of tritiated *trans*-2-pentene, propane, ethylene, and propylene. A radioactive product formed with a yield of 3.9 ± 0.1% could not be positively identified in the radio gas chromatographic analyses carried out

Table II. Yields of Tritiated Products from the Reactions of He^3H^+ Ions with Cyclopentane + 2 Mole % O_2 at 100 Torr

Tritiated product	Yield,[a] %
Methane	Not determined
Ethane	2.6 ± 0.1
Ethylene	4.1 ± 0.1
Propane	4.6 ± 0.4
Propylene	3.4 ± 0.2
trans-2-Pentene	4.5 ± 0.2
Cyclopentane	11.1 ± 0.4
Unknown[b]	3.9 ± 0.1
Total yield of organic tritiated products	34.2%

[a] See footnotes of Table I. [b] See text.

Chemistry Series, No. 58, the American Chemical Society, Washington, D. C., 1966, p 167.

[8] V. Aquilanti and G. G. Volpi, *J. Chem. Phys.*, **44**, 3574 (1966).

[9] F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 4272 (1967).

[10] P. Ausloos and S. G. Lias, *Discussions Faraday Soc.*, **39**, 36 (1965).

[11] P. Ausloos, private communication.

[12] R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **44**, 1641(1966).

with different columns. From its retention time, however, it could be a pentadiene.

The exothermic protonation of the cyclopentane by the helium tritide molecular ion, which represents the first step in the formation of the tritiated products

$$\mathrm{He^3H^+} + c\text{-}\mathrm{C_5H_{10}} \longrightarrow (\mathrm{C_5H_{11}}^*)^+_{\mathrm{exc}} + \mathrm{He} \qquad (11)$$

is formally analogous to the protonation of cyclopentane by the CH_5^+ ions observed by Field and Munson in the mass spectrometer.[9] The excited carbonium ions from reaction 11 can be collision stabilized at 100 torr

$$(\mathrm{C_5H_{11}}^*)^+_{\mathrm{exc}} + \mathrm{M} \longrightarrow \mathrm{C_5H_{11}}^{*+} + \mathrm{M_{exc}} \qquad (12)$$

and the stabilized ions can undergo a thermoneutral proton transfer to the inactive cyclopentane, according to process 13, which is likely to be the source of the observed C_5 products.

$$\mathrm{C_5H_{11}}^{*+} + c\text{-}\mathrm{C_5H_{10}} \longrightarrow \mathrm{C_5H_{10}}^* + \mathrm{C_5H_{11}}^+ \qquad (13)$$

The structure of the major tritiated $C_5H_{10}^*$ neutral product, the labeled cyclopentane isolated with a 11.1% yield, suggests that most of the stabilized carbonium ions from reactions 11 retain a cyclic structure. This can be regarded as a good evidence for the existence of the cyclopentanium ion. It may be observed in this connection that Field and Munson, in their mass spectrometric study of the protonation of cycloalkanes with CH_5^+ ions at 1 Torr,[9] while obviously unable to determine the structure of the protonated ion, observed relatively large intensities of the $(MW + 1)^+$ peak in compounds containing the cyclopentane ring.

The only tritiated C_5 olefin observed as a reaction product in the present study is *trans*-2-pentene, which represents, as in the case of *trans*-2-butene, the most stable among the linear isomers. A significant difference from the case of protonated cyclobutane is given, however, by the much smaller percentage of protonated cyclopentane ions that seem to rearrange to a linear structure.

The C_1–C_4 tritiated products arise from the fragmentation of the excited carbonium ions formed from reaction 11 which are not stabilized by collision at a pressure of 100 Torr. Ethane and ethylene can be directly formed from the fragmentation processes

$$(\mathrm{C_5H_{11}}^*)^+_{\mathrm{exc}} \longrightarrow \mathrm{C_3H_5}^{*+} + \mathrm{C_2H_6}^* \qquad (14)$$

$$(\mathrm{C_5H_{11}}^*)^+_{\mathrm{exc}} \longrightarrow \mathrm{C_3H_7}^{*+} + \mathrm{C_2H_4}^* \qquad (15)$$

While the formation of $C_3H_7^+$ ions in the protonation of cyclopentane with methanium ions at 1 Torr has been already observed in the mass spectrometer by Field and Munson,[9] the occurrence of a process corresponding to reaction 14 cannot be inferred from their data, since, apart from the different exothermicity of the protonation process, the ratio m/e 43 was the lower limit of mass range explored in their study.

The C_3-tritiated products, namely propane and propylene, are likely to arise from the exothermic hydride ion transfer from cyclopentane to the fragment ions formed in reactions 14 and 15

$$\mathrm{C_3H_5}^{*+} + c\text{-}\mathrm{C_5H_{10}} \longrightarrow \mathrm{C_3H_6}^* + \mathrm{C_5H_9}^+ \qquad (16)$$

$$\mathrm{C_3H_7}^{*+} + c\text{-}\mathrm{C_5H_{10}} \longrightarrow \mathrm{C_3H_8}^* + \mathrm{C_5H_9}^+ \qquad (17)$$

Cyclohexane. The yields of the tritiated products formed in the protonation of cyclohexane with He^3H^+ ions at 100 Torr are shown in Table III.

Table III. Yields of the Tritiated Products from the Reactions of He^3H^+ Ions with Cyclohexane + 2 Mole % O_2 at 100 Torr

Tritiated product	Yield,[a] %
Methane	Not determined
Ethane	1.2 ± 0.3
Ethylene	1.6 ± 0.1
Propane	2.7 ± 0.2
Propylene	3.0 ± 0.3
trans-2-Pentene	1.3 ± 0.2
trans-2-Hexene	3.1 ± 0.2
Cyclohexane	9.7 ± 0.9
Total yield of the tritiated organic products	22.6%

[a] See footnotes of Table I.

The spectrum of the products is similar to that observed in the protonation of cyclopentane, the higher yield being that of the parent hydrocarbon, in this case tritiated cyclohexane (9.7%), with considerably smaller yields of labeled *trans*-2-hexene, propylene, propane, ethylene, and ethane.

The protonation of cyclohexane by the helium tritide molecular ion is a strongly exothermic process

$$\mathrm{He^3H^+} + c\text{-}\mathrm{C_6H_{12}} \longrightarrow (\mathrm{C_6H_{13}}^*)^+_{\mathrm{exc}} + \mathrm{He} \qquad (18)$$

that yields excited carbonium ions, part of which are collision stabilized at a cyclohexane pressure of 100 torr

$$(\mathrm{C_6H_{13}}^*)^+_{\mathrm{exc}} + \mathrm{M} \longrightarrow \mathrm{C_6H_{13}}^{*+} + \mathrm{M_{exc}} \qquad (19)$$

and undergo a thermoneutral proton transfer with c-C_6H_{12}, to yield the observed tritiated C_6 hydrocarbons.

$$\mathrm{C_6H_{13}}^{*+} + c\text{-}\mathrm{C_6H_{12}} \longrightarrow \mathrm{C_6H_{12}}^* + \mathrm{C_6H_{11}}^+ \qquad (20)$$

Owing to the large excess of c-C_6H_{12}, reaction 20 causes the whole activity contained in the protonated species to be transferred to the C_6 hydrocarbons. The major C_6 product here is tritiated cyclohexane, whose formation can be hardly explained without the intervention of a cyclic protonated intermediate.

As in the case of cyclobutane and cyclopentane, we regard the present results as strong evidence in favor of the existence of the cyclohexanium ion.

Reaction 18 is analogous to the protonation of cyclohexane studied in the mass spectrometer by Field and Munson,[9] who employed the methanium ion as the protonating agent, working at a total CH_4 pressure of 1 Torr.

Field and Munson were obviously unable to determine the structure of the $C_6H_{13}^+$ ions from their observations in the mass spectrometer. However, they suggested that the formation of the $(MW + 1)^+$ ions in the cycloalkanes protonation could be explained by the fact that the cleavage of the C–C bond in the ring produced an ion with the same m/e ratio as in the C_nH_{2n+1} series.

$$\mathrm{CH_5}^+ + c\text{-}\mathrm{C_6H_{12}} \longrightarrow n\text{-}\mathrm{C_6H_{13}}^+ + \mathrm{CH_4} \qquad (21)$$

On the other hand, the results of the present study, where the actual isolation of the final, neutral products was achieved, strongly suggest, as previously pointed out, that at least a fraction of the $C_6H_{13}^{*+}$ ions formed from the protonation of c-C_6H_{12} with He^3H^+ ions retain a cyclic structure.

It should be fully realized, however, that great caution must be exercised in comparing the present results with those obtained by Field and Munson,[9] since (i) different protonating agents are involved, the reaction with He^3H^+ ions being much more exothermic; (ii) the reaction is carried out in different systems, and at largely different pressures (methane at 1 Torr *vs.* cyclohexane at 100 Torr). Despite such differences, however, the fraction of $C_6H_{13}^+$ ions which are collision-stabilized appears very close in both experiments, probably due to a fortuitous compensation of factors i and ii.

The isomerization of the protonated ions formed in reaction 18 and the subsequent thermoneutral proton transfer 19 lead to the formation of only one of the possible hexenes, namely the *trans*-2-hexene. This fact is of significance, since purely energetic reasons do not justify, in this case, the exclusive formation of this isomer, in view of the comparable stability of the *trans*-3-hexene. It seems likely that the selective formation of only one of the possible isomers is dictated by a precise mechanistic requirement of the isomerization process which leads from a cyclic to a linear carbonium ion.

The other tritiated products observed in the present study arise from the fragmentation of the excited carbonium ions formed in reaction 18

$$(C_6H_{13}^*)^+_{exc} \longrightarrow CH_4^* + C_5H_9^{*+} \qquad (22)$$

$$(C_6H_{13}^*)^+_{exc} \longrightarrow C_2H_6^* + C_4H_7^{*+} \qquad (23)$$

$$(C_6H_{13}^*)^+_{exc} \longrightarrow C_2H_4^* + C_4H_9^{*+} \qquad (24)$$

$$(C_6H_{13}^*)^+_{exc} \longrightarrow C_3H_6^* + C_3H_7^{*+} \qquad (25)$$

and the exothermic hydride ion transfer processes from c-C_6H_{12} to the fragment ions

$$C_5H_9^{*+} + c\text{-}C_6H_{12} \longrightarrow C_5H_{10}^* + C_6H_{11}^+ \qquad (26)$$

$$C_3H_7^{*+} + c\text{-}C_6H_{12} \longrightarrow C_3H_8^* + C_6H_{11}^+ \qquad (27)$$

It is interesting to note that, again, only one of the possible linear pentenes, namely the tritiated *trans*-2-pentene, is formed from reaction 26.

The fragmentation pattern of the excited $C_6H_{13}^{*+}$ ions, as determined by the spectrum of neutral products, is very similar, both qualitatively and quantitatively, to the fragmentation pattern following the protonation of both c-C_6H_{12} and c-C_6D_{12} with CH_5^+ ions, measured in the mass spectrometer by Field and Munson.[9] Reactions 22–25 were directly observed by these authors, while the hydride ion transfers 25 and 26 were definitely established by Abramson and Futrell[13] in their study on the ion–molecule reactions in cyclohexane, carried out with a tandem mass spectrometer.

Conclusions

The results of the present investigation support and extend the conclusions reached in a previous study on the protonation of cyclopropane with He^3H^+ ions[3] and may be summarized as follows.

(i) In the protonation of the lower cycloalkanes, from cyclopropane to cyclohexane, a fraction of the protonated carbonium ion retains a cyclic structure; in all the systems investigated, the present results suggest in fact the existence of gaseous cycloalkanium ions.

(ii) In all the systems investigated, a fraction of the protonated cycloalkane ions rearranges to a linear structure, the extent of the isomerization being comparable for the cyclopropanium, cyclopentanium, and cyclohexanium ions, while the protonated cyclobutane undergoes a much more extensive isomerization.

(iii) Normal tritiated alkanes are not formed in the protonation of the corresponding cycloalkanes. This finding is of interest, since it indicates that the linear alkyl ions (probably *sec*-alkyl ions) formed from the isomerization of the protonated cycloalkanes react according to the proton transfer

$$n\text{-}C_nH_{2n+1}^{*+} + c\text{-}C_nH_{2n} \longrightarrow n\text{-}C_nH_{2n}^* + C_nH_{2n+1}^+ \qquad (28)$$

which yields linear tritiated olefins, rather than undergoing the competing hydride ion transfer from the corresponding cycloalkane.

$$n\text{-}C_nH_{2n+1}^{*+} + c\text{-}C_nH_{2n} \longrightarrow n\text{-}C_nH_{2n+2}^* + C_nH_{2n-1}^+ \qquad (29)$$

This conclusion is supported by the results of Ausloos and Lias[10] and Borkowski and Ausloos,[14] who observed no hydride ion transfer from cyclopropane to *sec*-propyl ions, and from cyclobutane to *sec*-butyl ions.

(iv) Only the thermodynamically most stable *trans*-2 isomers, among the possible olefins, are formed from process 28. There is little doubt, however, that the reactions involved in these systems are kinetically controlled, and arguments based on thermodynamical considerations are of limited value. This is evident in the protonation of cyclohexane, where the exclusive formation of *trans*-2-hexene can only be explained by mechanistic considerations, owing to the comparable thermodynamic stability of *trans*-3-hexene.

(v) The present experiments do not provide direct evidence as to the way the $^3H^+$ becomes bounded to the cycloalkane to form the cycloalkanium ion. While edge-protonated structures, similar to those postulated by Olah and Lukas[15] for the low-temperature protonation of cycloalkanes in "magic" acid solutions, appear certainly possible, the isolation of tritiated cycloparaffins in systems at atmospheric pressure requires a considerably fast scrambling of the hydrogen atoms within the cycloalkanium ions, possibly by intramolecular hydride ion shifts.

A final remark stems from the trend of the combined yields of the tritiated organic products isolated in each system, which range from 67% in cyclopropane to 46% in cyclobutane, 34% in cyclopentane, and 23% in cyclohexane protonation.

The balance is provided, in each system, by the formation of an inorganic product, the hydrogen tritide, whose yield cannot unfortunately be determined with the necessary precision, owing to its presence, as a significant impurity, in the $^3H_2$ used to obtain the He^3H^+ ions. However, the measurements carried out confirm, from a qualitative standpoint, an increase of the yield of the organic products in the C_3 to C_6 cycloparaffins series. Such a trend is significant, since it suggests that the competition between the protonation process 1 and the hydride ion abstraction process 2 shifts in favor of the latter,[16] as one proceeds along the homologous series from c-C_3H_6 to c-C_6H_{12}.

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[13] F. P. Abramson and J. H. Futrell, *J. Phys. Chem.*, **71**, 3791 (1967).

[14] C. J. Borkowski and P. Ausloos, *J. Chem. Phys.*, **38**, 36 (1963).

[15] G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **90**, 932 (1968).

[16] Following a suggestion from Field and Munson,[9] related to behavior of the methanium ion, processes 1 and 2 may be regarded as the Brønsted acid (1) and the Lewis acid (2) reaction modes, respectively, of the He^3H^+ ion.