Reactions of Helium Tritide Ions with Gaseous Hydrocarbons. V. *cis*- and *trans*-1,2-Dimethylcyclopropane. Unambiguous Evidence for Gaseous Protonated Cyclopropanes

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Abstract: In order to gather direct chemical evidence for the occurrence of protonated cyclopropanes as intermediates in a gas-phase reaction, gaseous *cis*- and *trans*-1,2-dimethylcyclopropane were allowed to react with a gaseous Brønsted acid, the helium tritide ion formed from the β decay of molecular tritium. The cis and trans isomers gave the corresponding tritiated compounds retaining the configuration of the original molecules. The lack of any measurable cis–trans isomerization lends strong support to the view that the formation of the tritiated cycloalkanes, following the transfer of a triton from He^3H^+ to the substrate, proceeds *via* a cyclic intermediate, and does not involve the cleavage of the cyclopropane ring. These results corroborate the mechanistic interpretation of earlier experiments concerning the triton transfer from He^3H^+ to unsubstituted cycloalkanes, and provide unambiguous evidence for the intermediacy of protonated cyclopropanes in a gas-phase reaction.

In recent years, we focused our attention on the use of the helium tritide molecular ion, an exceedingly strong Brønsted acid conveniently obtained from the β decay of molecular tritium, as a reagent for the study of ionic processes in gases at atmospheric pressure. The scope, the experimental techniques, and the results of the investigations so far carried out on the reactivity of the He^3H^+ ion in gaseous arenes,[1] alkanes,[2,3] and cycloalkanes[3,4] were recently reviewed.[5]

The study of the gas-phase reactions of He^3H^+ with unsubstituted cycloalkanes provided what appeared to be fairly conclusive evidence for the intermediacy of gaseous cycloalkanium ions. In fact, the features of the reaction with gaseous cycloparaffins, in particular the formation of the correspondent labeled cycloalkanes in all the systems investigated, were consistent with a simple, two-step mechanism, involving the formation of a gaseous cycloalkanium ion, followed by the thermoneutral transfer of a proton to another molecule of substrate.

However, such straightforward interpretation was considerably weakened, at least as a rigorous argument for the intermediacy of gaseous protonated cyclopropanes, by the observation of Ausloos, Rebbert and Lias[6] that the loss of a proton from gaseous *n*-propyl ions leads to the formation of cyclopropane in addition to the expected propylene.

Taking into account the results of Ausloos and coworkers, the intervention of a gaseous cyclopropanium ion in the gas-phase attack of He^3H^+ on c-C_3H_6 cannot be safely deduced from the isolation of tritiated cyclopropane, since the latter could simply arise from the cyclization of a linear precursor, *i.e.*, the 1-propyl ion, formed in the exothermic tritonation.

In view of the ambiguity arising from the possibility of a recyclization reaction, it appeared highly desirable to address ourselves to a more detailed investigation of the problem, in the attempt to gather unambiguous evidence against the cleavage of the cyclic structure in any step of the reaction sequence initiated by the He^3H^+ attack on the cyclopropane ring and leading to the observed tritiated cyclopropanes.

In this and subsequent publications we wish to report on the results obtained from the study of the gas-phase reactions of the He^3H^+ ion with *cis*- and *trans*-1,2-dimethylcyclopropane.

Experimental Section

Materials. The isomeric dimethylcyclopropanes were prepared according to the procedure suggested by Doering and La Flamme[7] from the corresponding 1,1-dibromides, obtained according to the method described by Skell and Garner.[8] The crude cyclopropanes were purified by preparative gas chromatography over a 12-m diisodecyl phthalate column, operated at 70°.

Samples of propylene, cyclopropane, allene, butane, isobutane, *cis*- and *trans*-2-butene, isobutene, methylcyclopropane, 1,3-butadiene, *n*-pentane, isopentane, cyclopentane, cyclopentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and *cis*- and *trans*-2-pentene were obtained by commercial sources and used for identification purposes without further purification.

Samples of *cis*- and *trans*-1,3-pentadiene, methylenecyclobutane, and methylcyclobutane were prepared according to established procedures[9,10] and purified over a 13-m long squalane column, operated at 70°.

The stated purity of the $^3H_2$ exceeded 95% and was checked by gas-solid radiogas chromatography, using an 8 m long Al_2O_3–Fe_2O_3 column at $-194°$ for the analysis of hydrogen tritide[11] and a 3-m long 5-Å molecular sieve column for the analysis of tritiated methane.

Procedure. A tracer amount of molecular tritium was allowed to decay for periods ranging from 176 to 246 days within a gaseous system containing the organic substrate and oxygen, in the molar ratio 100/1, at total pressure of 300 Torr.

The samples were stored in sealed Pyrex ampoules, containing about 2 mCi of tritium in a total volume of 250 ml.

The analysis of the labeled products was carried out by radiogas chromatography, according to techniques described in detail

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elsewhere.[12,13] The following columns were employed: squalane, 13 m long, at 70°; dimethylsulfolane, 12 m long, at 50°; diisodecyl phthalate, 10 m long, at 50°; silica gel, 4 m long, at 100°.

Duplicate samples of each gaseous system, stored in separate ampoules, were analyzed on three different columns, each separation being carried out at least three times. The yields of the reaction products were obtained by dividing the activity contained in each product by the total activity of the He^3H^+ ions formed within the gaseous system during the storage period.

Results

The yields of the labeled products from the reactions of the He^3H^+ ions with gaseous *cis*- and *trans*-dimethylcyclopropane are listed in Table I. The standard deviations range from 5 to 10% of the values given, and the minimum activity detectable with the radiometric techniques employed corresponds to a yield below 0.5%. The analysis of the products from the *trans*-1,2-dimethylcyclopropane revealed the formation of an unknown tritiated compound, whose retention volumes were compared with those of authentic samples of the following hydrocarbons: propylene, cyclopropane, allene, *n*-butane, isobutane, 1-butene, *cis*- and *trans*-2-butene, isobutene, methylcyclopropane, butadiene, *n*-pentane, isopentane, 3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene, *cis*- and *trans*-2-pentene, *cis*- and *trans*-1,3-pentadiene, *cis*- and *trans*-dimethylcyclopropane, methylcyclobutane, methylenecyclobutane, cyclopentene, and cyclopentane. From the retention data, it appears that the labeled product, while definitely different from the linear pentenes and pentadienes and from methylcyclobutane, shows on the stationary phases employed a surprising similarity with cyclopentene. Unfortunately, the very low concentration of the labeled products, formed in amounts corresponding to *ca.* 10^{11} molecules, prevented the use of more conclusive identification techniques such as nmr, ir, or mass spectrometry.

Table I. Yields of Tritiated Products from the Gas-Phase Tritonation of *cis*- and *trans*-1,2-Dimethylcyclopropane with He^3H^+ Ions

Substrate	Tritiated products	Yield, %
cis-1,2-Dimethylcyclopropane	Methane	9.3
	cis-1,2-Dimethylcyclopropane	8.3
	2-Methyl-2-butene	8.3
	trans-2-Pentene	2.4
	Total yield of organic products	28.3
trans-1,2-Dimethylcyclopropane	Methane	6.7
	trans-1,2-Dimethylcyclopropane	8.3
	Unknown[c]	5.7
	(Unknown, after hydrogenation)	(5.7)
	Total yield of organic products	20.7

[a] All the experiments carried out at a pressure of 300 Torr and room temperature, in the presence of 2 mol % O_2. [b] Percentage of the total activity of the He^3H^+ ions formed within the system during the storage time. [c] See text.

Confirmatory evidence as to the nature of the unknown radioactive product was therefore sought through the following experiment. The mixture of tritiated products from the tritonation, added with inactive cyclopentene as a carrier, was resolved by preparative gas chromatography, and the recovered cyclopentene fraction containing the unknown labeled species was hydrogenated over a Pt/charcoal catalyst.

The analysis of the hydrogenated sample revealed the disappearance of the unknown radioactive compound, quantitatively converted into a product whose retention volume corresponded exactly to the value characteristic of cyclopentane. As a whole, the radiogas chromatographic evidence, before and after the hydrogenation of the unknown labeled product, strongly suggests its identification with tritiated cyclopentene, and definitely excludes its identification with the following products: linear pentenes and pentadienes, dimethylcyclopropanes, dimethylcyclopropenes, methylenemethylcyclopropane, methylcyclobutenes, and methylenecyclobutane.

Discussion

A. The Overall Yield of Organic Products. The combined yields of the labeled organic products from *cis*- and *trans*-dimethylcyclopropane account for only 28.3 and 20.7%, respectively, of the total activity of the tritonating reagent, the balance being essentially provided by the formation of hydrogen tritide.

The observation can be rationalized assuming, as in the case of alkanes[2,3] and unsubstituted cycloalkanes,[3,4] that the He^3H^+ undergoes, in addition to the Brønsted acid reaction

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

which leads to the formation of tritonated ions and eventually of tritiated hydrocarbons, a Lewis acid reaction, *i.e.*, the hydride-ion abstraction

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

which yields hydrogen tritide as the only *labeled* product.

A comparison with the yields of hydrogen tritide measured in the tritonation of cyclopropane, *ca.* 35%, reveals that the introduction of two methyl groups into the cyclopropane molecule considerably shifts the competition between reactions 1 and 2 in favor of the hydride-ion abstraction. The result qualitatively fits the trend prevailing in the tritonation of unsubstituted cycloparaffins, whose hydrogen tritide yields regularly increase along the homologous series from *ca.* 35% for $c\text{-}C_3H_6$ to *ca.* 75% for $c\text{-}C_6H_{12}$.

Incidentally, it may be worth mentioning that a similar trend was observed in a mass spectrometric investigation on the reactions of H_3^+, showing that the competition between protonation and hydride-ion abstraction is progressively biased in favor of the latter as one proceeds along the homologous series of alkanes.[14] Moreover, Ausloos and coworkers[15] established that the relative rate of hydride-ion transfer to alkyl ions regularly increases with the molecular weight of homologous cycloalkanes.

On the other hand, the relatively large difference in the H^3H yield from *cis*- and *trans*-dimethylcyclopropane shows that the competition between processes 1 and 2 does not exclusively depend on the molecular weight of the substrate, being heavily affected by structural factors as well. Similar positional and structural effects on the rate of hydride-ion abstraction from

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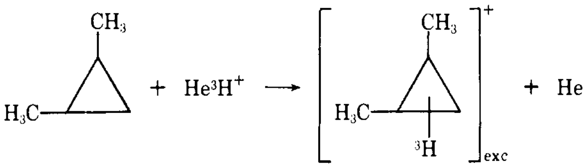
alkanes and cycloalkanes, and their correlation with the energetics of the process, were demonstrated in mass spectrometric[16] and radiolytic[15] studies of gaseous alkanes and cycloalkanes.

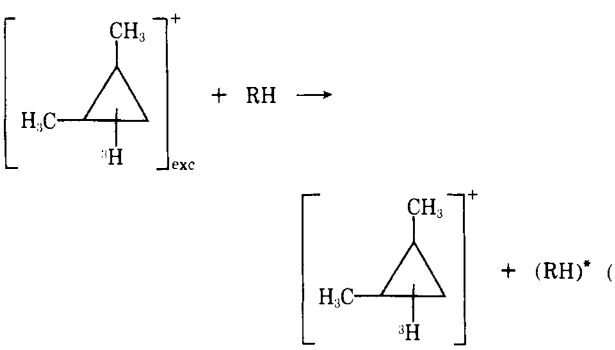
B. The Intermediacy of Gaseous Cyclopropanium Ions. From the data of Table I it is apparent that the tritonation of the isomeric dimethylcyclopropanes occurs with *retention* of the substrate configuration. The failure to detect any cis–trans isomerization shows conclusively that the labeled cycloalkanes isolated among the reaction products do not arise from the cyclization of a linear intermediate, which would necessarily yield a mixture of cis and trans isomers, as demonstrated, *inter alia*, by a number of investigations carried out in solution. The most pertinent example is provided perhaps by the work of Silver,[17] who isolated both *cis*- and *trans*-1,2-dimethylcyclopropane, in addition to the three possible amylenes, from the cyclization of the isopentyl ion in acetic acid.

The evidence now available strongly supports the mechanism suggested for the tritonation of the unsubstituted cyclopropane, based on the formation of a gaseous cyclopropanium ion



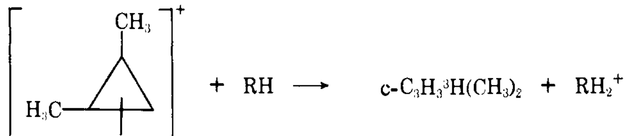
(1a)

followed by the collisional stabilization of a fraction of the excited intermediate in the hydrocarbon gas at 300 Torr



(3)

and by a thermoneutral proton transfer to another molecule of substrate



$c\text{-}C_3H_3{}^3H(CH_3)_2 + RH_2^+$

(4)

The suggested mechanism for the formation of labeled *cis*- and *trans*-1,2-dimethylcyclopropane from the corresponding inactive compounds involves three consecutive reactions closely analogous to well-established processes. There is little doubt that the reaction sequence is initiated by the exothermic triton transfer from He^3H^+, an exceedingly strong Brønsted acid, to the gaseous substrate.

Apart from the demonstrated ability of the same reagent to tritonate paraffins and unsubstituted cycloparaffins,[2–5] a close analogy can be found with the protonation (deuteration) of gaseous hydrocarbons with ArH^+, ArD^+, H_3^+, D_3^+, CH_4^+, CH_5^+, $C_2H_5^+$, CHO^+, and similar reagents, studied in the mass spectrometer[18–34] or with radiolytic techniques.[15,35–40]

The analogy can be further extended to the protonation of alkanes and cycloalkanes in $HFSO_3$–SbF_5 solutions, studied in detail by Olah and coworkers,[41–44] who demonstrated the occurrence of reactions similar to processes 1 and 2. The stabilization of highly excited gaseous ions with a limited number of internal degrees of freedom according to processes analogous to reaction 3 was repeatedly demonstrated in the mass spectrometric study of ion–molecule reactions, even at pressures well below 1 Torr.

Particularly pertinent examples are afforded by a mass spectrometric study by Aquilanti and Volpi,[32] who observed the partial stabilization of $C_3H_7^+$ ions (of unknown structure) from the protonation of c-C_3H_6 with H_3^+ in the pressure range 0.1–0.3 Torr, and by an investigation by Ausloos and Lias, who reported the stabilization of 2-propyl ions from the protonation of c-C_3H_6 with radiolytically produced H_3^+ in H_2 at atmospheric pressure.

Finally, thermoneutral proton-transfer reactions, corresponding to process 4, were frequently observed both in the mass spectrometer[23,45] and in solutions of strong acids.[46]

It should be explicitly pointed out that the isolation of *tritiated* dimethylcyclopropanes requires, before the quenching of the ion by the proton transfer 4, a fast equilibration of tritium within the gaseous cyclopropanium intermediate, a process often described in the solution chemistry of protonated cyclopropanes.[47]

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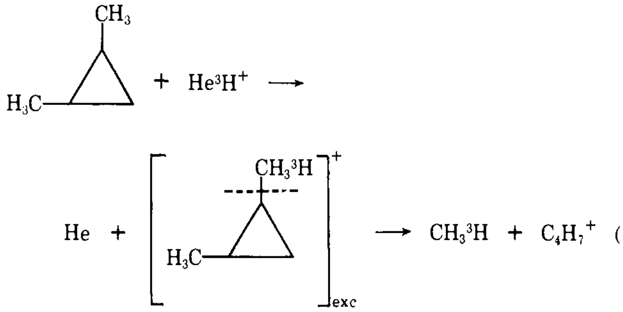
The results do not permit the assignment of a specific structure, *i.e.*, face tritonated, edge tritonated, or methyl bridged, to the cyclopropanium moiety.

However, the retention of configuration following the He^{3}H$^+$ attack rules out the intermediacy of linear pentyl ions and provides the first unambiguous evidence for the occurrence of the gaseous protonated cyclopropanes, often postulated on energetic grounds, or from the fragmentation pattern of isotopically labeled molecules, in a number of mass spectrometric investigations.[48–56]

C. The Fragmentation Products. The excited cyclopropanium ions that escape collisional stabilization undergo fragmentation processes leading to labeled products other than cyclopropanes. Tritiated methane is formed from both *cis*- and *trans*-dimethylcyclopropane, with yields of 9.3 and 6.7%, respectively. The most likely source of $CH_3{}^3H$ can be traced to the fragmentation of the excited cyclopropanium ions into a butenyl ion, $C_4H_7{}^+$, and methane, an energetically allowed process strictly similar to those observed in the gas-phase tritonation of the unsubstituted cycloalkanes with He^{3}H$^+$ [3–5] and in the mass spectrometric investigations on the protonation of cycloparaffins with $CH_5{}^+$ [30] and $H_3{}^+$.[32]

The butenyl ions formed from the fragmentation reaction are expected to undergo a hydride-ion abstraction from the substrate to yield butenes. Thus, the failure to isolate $C_4H_7{}^3H$ hydrocarbons among the reaction products *demands that the butenyl ions contain no tritium.*

The absence of the expected equilibration of the tracer between the two fragmentation products rules out a long-lived cyclopropanium ion as the precursor of $CH_3{}^3H$ and suggests that the reaction pathway leading to the formation of tritiated methane involves the attack of He^{3}H$^+$ on a methyl group of the substrate, followed by the fast dissociation of the methyl-tritonated intermediate.

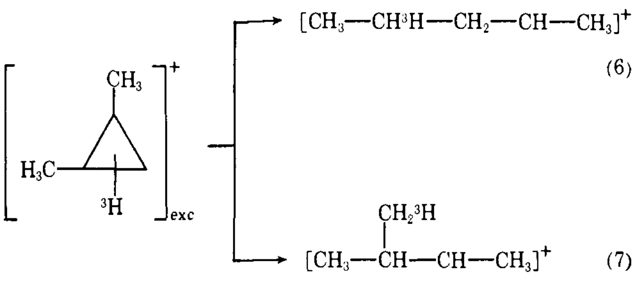


(5)

This interpretation is supported by the mass spectrometric data on the protonation of cycloalkanes with $CH_5{}^+$ reported by Field and Munson,[30] who observed a marked correlation between the intensity of the (M − 15) ion arising from the CH_4 detachment from the protonated species and the number of methyl groups available in the molecule of the substrate. The attack of the protonating reagent on the methyl groups of the substrate was also postulated by Olah and coworkers[44] in order to explain the formation of CH_4 in the protolytic cleavage of alkanes dissolved in $HFSO_3$–SbF_5 solutions.

Apart from the labeled methane and the tritiated parent, the other products from the tritonation of *cis*- and *trans*-dimethylcyclopropane are significantly different.

The cis isomer yields two linear amylenes, *i.e.*, *trans*-2-pentene and 2-methyl-2-butene, *via* the cleavage of the cyclopropane ring, a process to be regarded as a particular fragmentation pathway of the excited cycloalkanium ion.



(6)

(7)

The linear amyl ions from processes 6 and 7 can subsequently undergo a proton transfer to another molecule of substrate, forming the labeled pentenes. The thermodynamically most stable 2-methyl-2-butene is formed in a considerably higher yield than is *trans*-2-pentene, while isomeric *cis*-2-pentene and 1-pentene are not formed at all, in agreement with the results of earlier investigations, showing that only the most stable among the isomeric olefines are formed from the cleavage of gaseous tritonated cycloalkanes.[4]

On the other hand, the failure to isolate tritiated 2-methyl-1-butene, whose thermodynamic stability is intermediate between those of 2-methyl-2-butene and *trans*-2-pentene, underlines the influence of kinetic and structural factors on the course of the reaction.

In striking contrast with the behavior of the cis isomer, *trans*-1,2-dimethylcyclopropane yields no labeled amylenes, and the only tritiated species isolated among the reaction products in addition to the labeled substrate and to $CH_3{}^3H$ was tentatively identified as cyclopentene, on the grounds of chemical and radiogas chromatographic evidence. From the lack of conclusive identification of the tritiated product, and in view of the unusual, if interesting, rearrangement required for a C_3–C_5 ring expansion in a gaseous ion, the present results must await forthcoming confirmation and extension before a mechanism for cyclopentene formation can be suggested.

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