

Reactions of Electrophiles with Bromocyclopropane; a Nuclear Decay Study

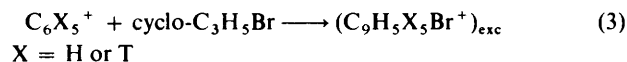
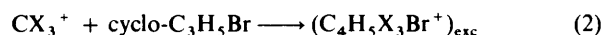
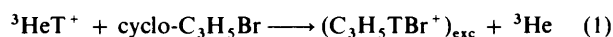
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The gas-phase reactions of ${}^3\text{HeT}^+$, CX_3^+ , and C_6X_5^+ ($\text{X} = \text{H}$ or T), produced by β^- decay, with cyclopropyl bromide were studied by analysis of the radioactive neutral products. Competition between the ring and the bromine atom as reaction sites was observed. A comparison with previous gas-phase and condensed-phase studies is given.

The three-membered carbon ring is a basic system. Theoretical models¹ predict that olefins and their cyclopropane analogues behave similarly towards electrophiles, and solution studies² support this view. However, in the gas phase, where reactions are unaffected by factors such as solvation and ion pairing, the scanty experimental evidence³ shows that the proposed models do not describe in full the properties of the cyclopropane ring. To gain further insight into this topic it seemed useful to compare the reactivity of the cyclopropane ring with that of functions other than the carbon-carbon double bond. A method of choice would be to study the gas-phase intramolecular selectivity for reactions of positively charged species with monosubstituted cyclopropanes. For this purpose, cyclopropyl bromide was considered particularly appropriate, as it also contains an n basic centre, and some condensed-phase data are available for comparison. Previous work has shown that cyclopropyl bromide behaves differently towards electrophiles such as the proton and the methyl cation in a way which depends on environmental factors and on the nature of the reactants.^{4,5}

We report here new ionic processes undergone in the gas phase by cyclopropyl bromide and positively charged electrophiles of well defined structure formed by spontaneous β^- decay of multitruncated precursors.⁶ Our approach allowed us to employ ions not easily accessible by other techniques; equations (1)–(3) represent the reactions investigated. In addition, a liquid-phase study of reaction (3) is reported and discussed.



Experimental

Materials.—Bromocyclopropane (Merck-Schuchardt) was purified by preparative g.l.c. (Porapak Q column) and analysed by mass spectrometry.^{5c} Ammonia and helium (Matheson), oxygen (SIO), and *t*-butylamine (Merck) were research-grade chemicals and used as received. Tritium gas was purchased from the Radiochemical Centre, Amersham. Multitruncated methane⁷ and benzene⁸ were kindly supplied by the scientists who synthesized them.

Sample Preparation.—In the gas-phase experiments, Pyrex bulbs (0.25–1 l) were connected to a vacuum line, outgassed, filled with the desired gases, and sealed. Bromocyclopropane and labelled benzene were added as liquids contained in small,

fragile Pyrex ampoules which were broken by shaking the bulbs. Tritium and labelled methane were allowed to diffuse into the bulbs from sealed vials.⁹ In the liquid-phase experiments multitruncated benzene and cyclopropyl bromide were mixed in Pyrex vials, which were sealed after freezing under oxygen.

Growth of Decay Products.—Activity ranging from 1 to 2 mCi was present in each sample, which was stored in the dark at room temperature for about 12 months. Ion-molecule reactions between the daughter ions and inactive hydrogen, methane, and benzene, in which the labelled compounds were diluted, were regarded as highly unfavourable because of dilution factors, and their contribution was disregarded. Also radiolytic effects were disregarded, because of the low dose delivered to the bulk by β^- decay irradiation. Blank radiolytic experiments, carried out with an external γ -source, supported the foregoing conclusions.

Analysis.—Flow radio-g.l.c.¹⁰ was used to detect the radioactive products. A Carlo Erba instrument, model 410, equipped with HWD detector and an ionization chamber or an internal-flow proportional counter, was employed. The aliphatic products were determined by use of a Porapak Q column,^{5a,b,9,11} and the aromatic products with an IGEPAL ICO-880 or Bentone 34/SP 1200 column.^{3d} The products were identified by comparison of retention volumes with those of authentic samples, and their quantities were measured from peak areas. The yields were calculated as percent radioactivity due to T , CX_3 , and C_6X_5 ($\text{X} = \text{H}$ or T) in the products relative to the radioactivity due to all the HeT^+ , CX_3^+ , and C_6X_5^+ daughter ions after correction for isotopic composition, when necessary.

Results

The yields of the radioactive organic products formed in the gas phase by the attack of HeT^+ , CX_3^+ , or C_6X_5^+ on cyclopropyl bromide are reported in Table 1, together with the experimental conditions. Table 2 lists the data relating to phenylium ion experiments in the liquid phase. The ionic character of the processes under investigation was ensured by the presence of oxygen, a good scavenger of thermal radicals, and confirmed by the decrease in the yields caused by the presence of a scavenger of positive ions (ammonia or *t*-butylamine). The recovered total activity was generally low, probably because of the formation of compounds which are not eluted from the g.l.c. columns, e.g. TBr in ${}^3\text{HeT}^+$ experiments. However, hydride-ion transfer from bromocyclopropane to the attacking ions may form tritiated molecules not distinguished from the radioactive starting materials. At least two independent samples were prepared and analysed several times. The

Table 1. Gas-phase ${}^3\text{HeT}^+$, CX_3^+ , and C_6X_5^+ ($\text{X} = \text{H}$ or T) attack on cyclo- $\text{C}_3\text{H}_5\text{Br}$

Ion	System composition ^a			Radiochemical yields (%) ^b				
	cyclo- $\text{C}_3\text{H}_5\text{Br}$ P/Torr	He P/Torr	NH_3 P/Torr	CH_3Br	$\text{C}_2\text{H}_5\text{Br}$	cyclo- $\text{C}_3\text{H}_5\text{Br}$	$\text{C}_6\text{X}_5\text{Br}$	Total
${}^3\text{HeT}^+$	1.0	80			0.06	0.27		0.33
${}^3\text{HeT}^+$	1.0	80	3		0.02	0.03		0.05
CX_3^+	1.0	100		28 ^c	70 ^c			98
CX_3^+	1.0	100	5	5 ^c	21 ^c			26
C_6X_5^+	0.8	100					8.0 ^c	8.0
C_6X_5^+	1.7	100	3				0.7 ^c	0.7

^a O_2 10%; 1–2 mCi of starting tritiated compounds. ^b Relative to daughter decay ions. ^c Yields corrected for isotope composition.

Table 2. Liquid-phase C_6X_5^+ ($\text{X} = \text{H}$ or T) ion attack on cyclo- $\text{C}_3\text{H}_5\text{Br}$

System composition ^a		Radiochemical yields (%) ^b		
cyclo- $\text{C}_3\text{H}_5\text{Br}$ (mg)	$\text{t-C}_4\text{H}_9\text{NH}_2$ (mg)	iso- $\text{C}_3\text{H}_7\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{Br}$	Total
600		1.2	65.0	66.2
600	4	0.1	5.0	5.1

^a Oxygen-saturated. ^b Relative to daughter decay ions, corrected for isotope composition.

Table 3. Yields and heats of formation of the most abundant ions from the decay of tritiated hydrogen, methane, and benzene molecules

Molecule	Daughter ion	Yield (%)	Heat of formation (kJ mol ⁻¹)
HT	${}^3\text{HeT}^+$	90 ^a	ca. 1 300
CH_3T	CH_3^+	82 ^b	1 078—1 212 ^d
$\text{C}_6\text{H}_5\text{T}$	C_6H_5^+	72 ^c	1 246—1 347 ^d

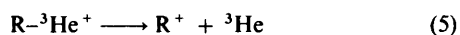
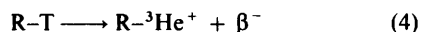
^a From ref. 12. ^b From ref. 13. ^c From ref. 14. ^d With the contribution of excess of vibrational energy.

reported data are mean values of all the measurements and were reproducible within a standard deviation of 10% except for the lowest values (which may be less precise).

In the gas phase, only bromine-containing products are formed, and, remarkably, in the experiments with HeT^+ H/T exchange, with retention of the original structure, is observed. In contrast, the formation of a noticeable amount of a hydrocarbon (isopropylbenzene) is a distinguishing feature of the reactions of phenylum ion in the liquid phase.

Discussion

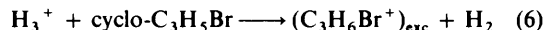
Production of the Reagent Ions.—The chemical consequences of β^- decay in a tritiated molecule can be traced to the formation of a positively charged species [equation (4)]. Only



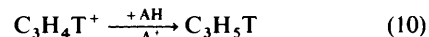
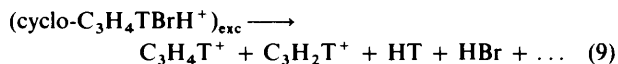
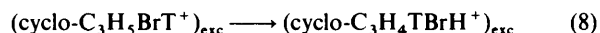
for $\text{R} = \text{H}$, D , or T is the ${}^3\text{He}$ atom chemically bonded; in all the other cases dissociation occurs in a few vibrations, mainly according to equation (5). Table 3 lists the yields of the most abundant ions originating from the molecules used in this work, as determined by mass spectrometric analysis.^{12–14} Provided that more tritium atoms are present in the parent molecule, R^+ still bears a radioactive label and has no electronic or translational excess of energy, but it can possess some

vibrational energy as a result of structural changes when passing from the neutral state to the ionic one.¹⁵ The pertinent thermochemical values are reported in Table 3.

Reactions of ${}^3\text{HeT}^+$.—The 'protonating' ability of ${}^3\text{HeT}^+$ is well documented.^{6a,b} Although all the pertinent data are not available, the enthalpy change for reaction (1) can be related to that estimated^{5c} for reaction (6) through the relationship $\Delta H_1 < \Delta H_6 \leq -290 \text{ kJ mol}^{-1}$ and the difference in the heats of

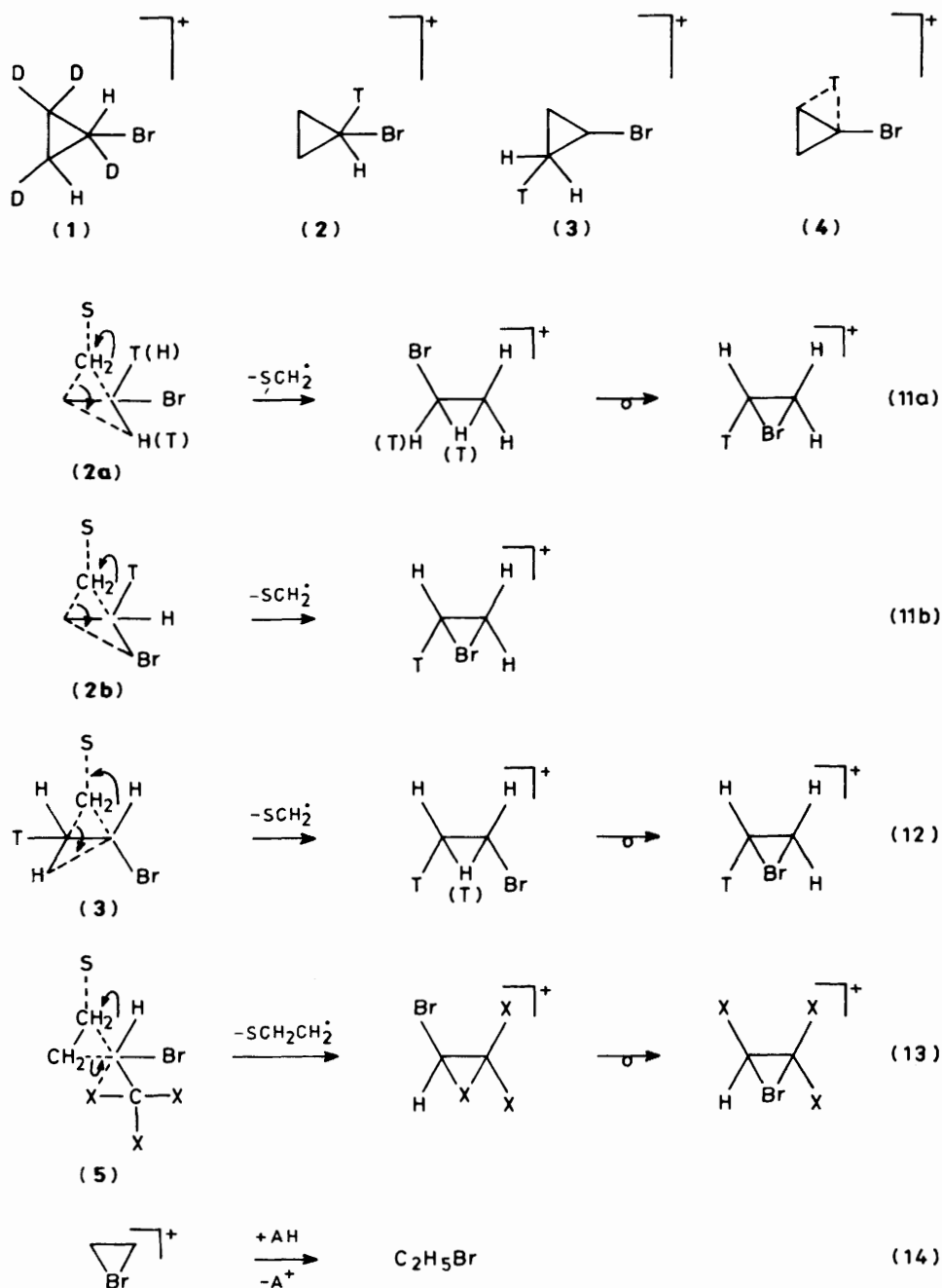


formation of ${}^3\text{HeT}^+$ (see Table 3) and H_3^+ [$\Delta H^\circ(\text{H}_3^+) = 1 078 \text{ kJ mol}^{-1}$]. Therefore, we conclude that reaction (1) is thermochemically allowed. A hydrogen chemical ionization mass spectrometric (H_2 -c.i.m.s.) study^{5c} showed that protonation of bromocyclopropane induces HBr elimination as the major process and leads to the formation of C_3 ions. In the present experiments TBr elimination [equation (7)] yields unlabelled C_3 ions. As a consequence, H/T scrambling between



bromine and the ring, as in equation (8), is ruled out; otherwise, labelled hydrocarbons, originating from labelled carbocations, e.g. in reactions (9) and (10), would have been found. For the foregoing reason neutralization *via* proton transfer from cyclo- $\text{C}_3\text{H}_4\text{TBrH}^+$ is not the likely route to tritiated cyclopropyl bromide. The recovery of the latter makes direct attack on the ring conceivable; thus it appears the carbon skeleton is able to compete with bromide for triton without losing its structural features.

The presence of ethyl bromide among the products provides evidence of the fragmentation of the condensation complex, excited by the exothermicity of the tritination reaction (1). The ion cyclo- $\text{C}_3\text{H}_5\text{TBr}^+$ is formally analogous to the species involved in the electrophilic bromination of cyclopropane in the liquid^{16,17} and in the gas phase.¹⁸ In superacidic solution,¹⁷ considerations based on stereochemistry supported attack at a ring atom and the formation of the ion (1). Attack by ${}^3\text{HeT}^+$ could yield the isomeric intermediates (2)–(4). Proton loss from (2) or (3) is the direct route to cyclo- $\text{C}_3\text{H}_4\text{TBr}$. Ring opening of excited (2) or (3), possibly concerted with internal Br



Scheme 1. Edge attack of ${}^3\text{HeT}^+$ and CX_3^+ ($\text{X} = \text{H}$ or T) on bromocyclopropane

or H(T) attack,¹⁹ respectively, and CH_2 transfer to a suitable acceptor, *e.g.* oxygen, would yield ethylbromonium ion as the precursor of ethyl bromide. Scheme 1 shows the proposed mechanistic implications for the rearrangement processes. The results are also consistent with the participation of the edge-tritiated ion (4); however, (2) or (3) must be involved to account for H/T exchange on the ring, necessary for the formation of the labelled substrate. Attack on C-1 seems to be preferred, as a unifying picture of ${}^3\text{HeT}^+$ and CX_3^+ reactions emerges (see later).

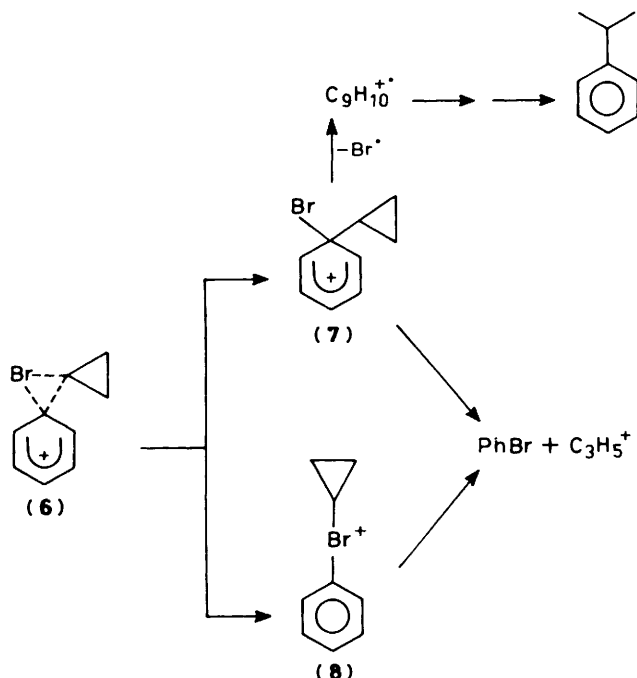
When drawing analogies between our results and those obtained from other studies, one must take into account differences in environmental conditions and in the method of generating the reactants. Even so, comparisons between our work and that carried out with electrophilic brominating agents

in the gas phase¹⁸ are not readily made. In fact, the ill-defined nature and energetics of the nucleogenic brominating agents²⁰ compare unfavourably with our systems and even more with solution results.

Reactions of CX_3^+ .—The enthalpy change in reaction (2) can be evaluated as $\Delta H_2 \leq -234 \text{ kJ mol}^{-1}$ from the limiting conditions $\text{MCA}(\text{RY}) \leq \text{MCA}(\text{HY})$, ($\text{R} = \text{alkyl}$, $\text{Y} = \text{halogen}$),²¹ where $\text{MCA}(\text{S})$ is defined as $-\Delta H_{15}$. Decay-produced methyl cations can have some vibrational excitation which contributes to the exothermicity of CX_3^+ attack, and in

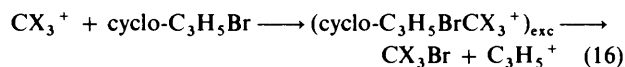


Table 3 pertinent values are shown. The formation of methyl



Scheme 2. Phenylum ion attack on bromocyclopropane

and ethyl bromides is evidence for two reaction sites, *viz.* bromine and the ring. Thus, in addition to the bromide-abstraction process (16), reaction (13) in Scheme 1 is proposed

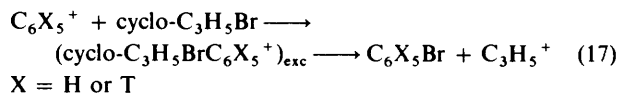


to account for the formation of labelled ethyl bromide *via* the excited species (5). The higher yield of ethyl bromide reflects the higher reactivity of the carbon skeleton towards methyl cation as compared with that of bromine. Edge methylation on C-1 accounts for the cyclization of the incipient bromoethyl cation,¹⁹ possibly in a concerted way, to the very stable²² ethylenebromonium ion. The absence of products other than methyl and ethyl bromide and the very high total radiochemical yield (96%) support the proposed mechanisms.

It is interesting to compare the course of attack of ${}^3\text{HeT}^+$ and CX_3^+ on the ring. Essentially, proton and triton transfer from (2) and (3) are thermochemically equivalent; however, proton and CX_3^+ elimination from (4) are not thermochemically equivalent, and as expected, only ${}^3\text{HeT}^+$ causes E-for-H (E = T or CX_3) substitution. From the nature of the products shown in Table 1 it can be concluded that Br^+ and Br elimination²³ do not compete favourably with proton (triton) and CX_3^+ loss. The formation of ethylenebromonium ion provides the driving force for the processes in Scheme 1, and suitable moieties (CH_2 and C_2H_4 for ${}^3\text{HeT}^+$ and CX_3^+ attack, respectively) are eliminated. Loss of CH_2 from (4) is not observed, in agreement with the fact that the formation of propyl bromides requires the intermediacy of species of energy higher than that of ethylenebromonium ion.²² Edge attack on C-1 provides a further feature common to ${}^3\text{HeT}^+$ and CX_3^+ reactions, although the occurrence of reactions (13) cannot be excluded. It is interesting to compare the present results with those obtained with the ions $\text{CH}_3\text{FCH}_3^+$ and $\text{CH}_3\text{ClCH}_3^+$.⁵ Dimethylfluoronium and methyl cations prefer to attack the ring, whereas dimethylchloronium ions and protons (tritons) attack bromine, as shown by the extent of bromide abstraction. This behaviour can be attributed to the similar structural parameters and charge distribution of CH_3 in $\text{CH}_3\text{FCH}_3^+$ and CX_3^+ .²⁴

Reactions of Phenylum Ion.—The distinguishing feature of phenylum ion lies in the two reaction centres represented by the empty σ orbital and the π system. The evaluation of structural and thermochemical parameters associated with the species produced in the decay event has established that phenylum ion can possess some vibrational energy,^{15a,c} which contributes to the exothermicity of reaction (3).

The gas-phase experiments reported in Table 1 are characterized by the occurrence of bromide abstraction (17) as the only



detected process. This observation prompted us to investigate the system also in the liquid phase, to discover whether solvation affects the formation of products. When tritiated benzene decays in liquid bromocyclopropane (see Table 2), the total yield of recovered products increases, and significant amounts of isopropylbenzene are formed. However, bromide abstraction is still the major process. The behaviour of phenylum ion is rationalized in Scheme 2 by considering its ability to form the Wheland-like complex (6), where the excitation energy and the charge associated with electrophilic attack [reaction (3)] are delocalized over the aromatic ring. After reorganization of (6) to give (7) and/or (8), C_3H_5^+ loss provides a direct route to bromobenzene. Loss of Br^+ ²³ from (7) leaves a $\text{C}_9\text{H}_{10}^{+\cdot}$ radical cation, which in the liquid phase is stabilized by solvation and undergoes further (as yet unclear) processes leading to isopropylbenzene; in the gas-phase it decomposes to products indistinguishable from the benzene precursor and naturally occurring decay fragments.

Although the present experiments do not indicate the relative importance of structures (7) and (8), nevertheless, after the early negative results of Dence and Roberts,²⁶ this seems the first case where the formation of a phenyl(cyclopropyl)halogenonium ion can be postulated on the basis of experimental evidence.

Conclusions

In the gas phase the nucleophilic properties of the cyclopropane ring are evidenced by the competition in cyclopropyl bromide of the carbon skeleton and the bromine atom for positively charged species of well defined structure. The nuclear decay technique provides the means to generate ions not easily available by other methods and to widen the reactivity of bromocyclopropane in electrophilic reactions.

Depending on the nature of the reagent and the experimental conditions, the extent of competition between the bromine centre and the three-carbon ring varies. However, in view of both the present and previous results it can be concluded that the cyclopropane ring undergoes a distinct electrophilic attack, as demonstrated by analysis of ionic transients and neutral products. Therefore, the different behaviours of bromocyclopropane observed in superacidic media can be regarded as limiting cases, *i.e.* the results of the effects produced by environmental factors and the particular nature of the 'magic' reactants.⁴

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Received 12th November 1985; Paper 5/1991