Reactions of Recoil ^{80}Br Activated by the (n, γ) Process with Some Gaseous Cyclanes (C_4—C_6)

Masakatsu Saeki and Enzo Tachikawa
Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-Mura, Ibaraki 319-11

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The reactions of ^{80}Br from the (n,γ) process with cyclanes (C_4—C_6) have been systematically investigated. The primary products formed by the ^{80}Br-for-H reaction were excited and underwent at least two modes of unimolecular decomposition. One was the elimination of the H^{80}Br molecule, and the other was the cleavage of the ring, giving the corresponding bromo-olefin and olefin. The former process was important particularly in the lower-pressure end. Thus, the reaction was easily suppressed by increasing the pressure. However, the latter process showed a different feature; that is, the yields of the decomposition products stayed at an almost constant level over the whole pressure range studied. This indicates that a highly excited product decomposes preferentially through a ring-cleavage reaction. When the total organic yield from each reaction system was plotted against the carbon number of the reactant molecules, a linear correlation was obtained. After some possible consideration, it was concluded that the life of the intermediate complex might play a more important role in the reaction of ^{80}Br with cyclanes than the other factors. Some considerations about the radiolysis of the reactant molecule are also mentioned.

The primary products formed by hot atom reactions are usually excited by the kinetic energy introduced by the recoil atoms and undergo a subsequent decomposition. Studies of these decomposition processes are one of the methods which can be used to obtain information on the energetics of hot atom reactions.

In a previous paper[1] we investigated the unimolecular decomposition of excited (c-$C_3H_5{}^{80}Br$)* formed by the reaction of ^{80}Br from the (n, γ) process with cyclopropane (c-C_3H_6) and with bromocyclopropane (c-$C_3H_5{}^{80}Br$). The results showed that the median excitation energy of the primary product from the ^{80}Br-for-H reaction was higher than that from the ^{80}Br-for-Br reaction. It was also deduced that the rupture of the C–Br bond as part of the decomposition processes of the excited primary products is more important in the ^{80}Br-for-Br reaction than in the ^{80}Br-for-H reaction.

In the present work we investigated the reactions of ^{80}Br from the (n, γ) process with gaseous cyclanes of cyclobutane, cyclopentane, and cyclohexane (c-C_4H_8, c-C_5H_{10}, and c-C_6H_{12}); the stability of the ring increases in that order. The work has two prime objects. One is the determination of the relative importance of the ring-cleavage and the HBr-elimination in the decomposition of the primary products from these reactant molecules. The other is to clarify the systematics in the reactivities of cyclanes with the recoil bromine. For these purposes, the total organic yields at high pressures were carefully investigated.

Experimental

Materials. The target chemicals, c-C_4H_8, c-C_5H_{10}, and c-C_6H_{12}, were supplied by the Merck Sharp Co., the Tokyo Chem. Co., and the Nippon Rikagakuyakuhin Co. respectively. Their nominal purities are more than 99% for c-C_4H_8 and c-C_5H_{10} and more than 95% for c-C_6H_{12}. They were purified by means of an ordinary vacuum distillation method before use. The source molecules of the hot bromine atom, CF_3Br and CH_3Br, were purchased from the Matheson Co. and the Tokyo Chem. Co. The other reagents used, H_2S, O_2, Br_2, and I_2 were all of the highest purity available.

Sample Processing A quartz ampoule with a breakable seal was used as the reaction vessel. The required gases were placed in the ampoule utilizing a vacuum line. The CF_3Br was used as the source molecule for the c-C_4H_8 and c-C_5H_{10} systems, whereas CH_3Br was used for the c-C_6H_{12} system.

The JRR-4 reactor in JAERI was used as the neutron source. Samples were irradiated for 10—40 s in the T pipe, where the thermal neutron flux was 3×10^{12} n cm^{-2} s^{-1}.

Within 15 min after the end of irradiation, the irradiated samples were injected directly into a radio-gas chromatograph by the help of a vacuum line. The separation columns used were DOP column, Neopak 1A of 60/80 mesh coated with 15% dioctyl phthalate, and a silicone column, Shimalite C of 30/80 mesh coated with silicone DC 550+stearic acid. The DOP and silicone columns, both 5 m long, were used for the c-C_4H_8 and c-C_5H_{10} systems and a short DOP column, 2.8 m, for the c-C_6H_{12} system. In the operation, the temperature of the columns was raised from room temperature to 115 °C at the rate of 8 °C min^{-1}.

The products were usually identified by comparing their retention times with those of commercial bromides. When the compounds will not be commercially available, the products were identified by applying a relationship between the boiling points and the retention times previously established[1] Furthermore, the unsaturated products, such as CH_2-$CHCH_2Br$ and C_4H_7Br, were assigned on the basis of the vanishing of their radioactivities in the radiochromatogram upon the addition of inactive Br_2 to the sample after its irradiation.

The absolute yields of the products were determined by a comparative method, using Ar as the internal standard; the details of the method were described elsewhere.[1]

Results

c-C_4H_8 System. In the reactions of ^{80}Br with c-C_4H_8, we added as a scavenger O_2, H_2S, I_2, or a mixture of H_2S+O_2. The chief products were c-C_4H_7-^{80}Br, $CH_2CH^{80}Br$, $CH_3{}^{80}Br$ and $C_4H_7{}^{80}Br$.[2] As minor products, $C_2H_5{}^{80}Br$, i-$C_3H_7{}^{80}Br$, n-$C_3H_7{}^{80}Br$, and others were also detected. When the scavenger was changed from the above substances to Br_2, however, the unsaturated products disappeared and some polybromo-products, such as $CH_2BrCH_2{}^{80}Br$, $CH_2{}^{80}BrBr$, and $CH^{80}BrBr_2$, became detectable.

From careful studies of the scavenger effects of O_2, H_2S, I_2, H_2S+O_2 or Br_2, it was concluded that the 2 : 3 mixture of H_2S and O_2 was the most suitable additive to suppress the thermal reaction of ^{80}Br. The scavenger of Br_2 made the unsaturated products undetectable. In the I_2 scavenging experiments, the identification of the products became difficult, because some products labelled by ^{128}I were also produced. The amount of O_2 or H_2S sufficient for the complete suppression of thermal reactions far exceeded 10 mol % of the reaction system. Thus, in the subsequent experiments, the mixture of H_2S and O_2 was used as the scavenger.

Table 1 shows the percent yields of the products at the system pressure of 600 Torr (1 Torr = 133.3 Pa); the compositions of the gases are also given in the table. The products have been grouped into two different categories; one, the scavenger-insensitive group, includes $CH_2CH^{80}Br$, $C_4H_7{}^{80}Br$, i-$C_4H_9{}^{80}Br$, and c-$C_4H_7{}^{80}Br$, while the other, the scavenger-sensitive group, includes $CH_3{}^{80}Br$, $C_2H_5{}^{80}Br$, i-$C_3H_7{}^{80}Br$, and n-$C_3H_7{}^{80}Br$. The yields of the products in the latter group and that of $CH_2CH^{80}Br$ showed no clear pressure-dependence and were constant at the values shown in Table 1 within an experimental uncertainty from 151 to 798 Torr. On the contrary, the yields of all the products in the former group except $CH_2CH^{80}Br$ showed a rather significant dependence on the system pressure from 151 to 798 Torr: from 0.27 to 0.6% for $C_4H_7{}^{80}Br$, from 0.05 to 0.15% for i-$C_4H_7{}^{80}Br$, and from 1.84 to 2.42% for c-$C_4H_7{}^{80}Br$.

Due to the limitation of the vapor pressure of c-C_4H_8, the system pressure above 800 Torr was only attained by adding ethane as a pressure-builder; *e.g.*, four times as much ethane as c-C_4H_8 were added to the reaction system. Figure 1 shows the dependences of the c-$C_4H_7{}^{80}Br$ and $CH_2CH^{80}Br$ yields on the system pressure with and without a pressure-builder. In the presence of ethane, the $CH_2CH^{80}Br$ yield was already corrected for the small amount of that from ethane according to the method to be described in the next section.

TABLE 1. ABSOLUTE YIELDS OF PRODUCTS IN THE c-C_4H_8 SYSTEM

Product	Yield (%)
$CH_2CH^{80}Br$	0.93±0.04
$C_4H_7{}^{80}Br$	0.66±0.12
i-$C_4H_9{}^{80}Br$	0.19±0.04
c-$C_4H_7{}^{80}Br$	2.24±0.03
$CH_3{}^{80}Br$	0.31±0.02
$C_2H_5{}^{80}Br$	0.09±0.01
i-$C_3H_7{}^{80}Br$	0.06±0.01
n-$C_3H_7{}^{80}Br$	0.10±0.02

Composition of gases

c-C_4H_8	: 520 Torr
CF_3Br	: 10 Torr
$H_2S + O_2(2:3)$	: 60 Torr
Ar	: 10 Torr
Total pressure	: 600 Torr.

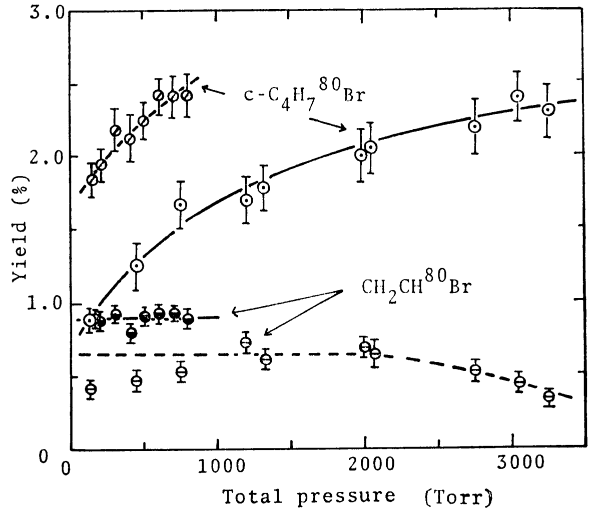

Fig. 1. Pressure-dependences of main products in c-C_4H_8 system.
In the presence of ethane; ⊙: c-$C_4H_7{}^{80}Br$,
⊖: $CH_2CH^{80}Br$.
In the absence of ethane; ⊘: c-$C_4H_7{}^{80}Br$,
◒: $CH_2CH^{80}Br$.

c-C_5H_{10} System. In the c-C_5H_{10} system, the mixture of H_2S and O_2 was also used as a scavenger. The products in this system are c-$C_5H_9{}^{80}Br$, $CH_2CH^{80}Br$, $CH_2CHCH_2{}^{80}Br$, $CH_3{}^{80}Br$, and $C_4H_7{}^{80}Br$.[2] The percentage yields of these products at 400 Torr are listed in Table 2, along with the experimental conditions. Figure 2 shows the yield variations in c-$C_5H_9{}^{80}Br$, $CH_2CHCH_2{}^{80}Br$, and $CH_2CH^{80}Br$ as a function of the pressure. Ethane was also added to the reaction system as a pressure-builder in the proportion of 4 to 1. Among these products, c-$C_5H_9{}^{80}Br$ is the only product showing a pressure dependence; the yield increases significantly with the pressure at the beginning and then tends to level off.

c-C_6H_{12} System. In order for one of the main products, c-$C_6H_{11}{}^{80}Br$, to elute with a reasonable retention time, a short DOP column (2.8 m) was used for this system. Unfortunately, this column did not provide a quantitative separation of Ar and CF_3Br. Thus, the source molecule was converted from CF_3Br

TABLE 2. ABSOLUTE YIELDS OF PRODUCTS IN THE c-C_5H_{10} SYSTEM

Product	Yield (%)
c-$C_5H_9{}^{80}Br$	0.76±0.10
$CH_2CH^{80}Br$	0.23±0.03
$CH_2CHCH_2{}^{80}Br$	0.30±0.03
$CH_3{}^{80}Br$	0.16±0.02
$C_2H_5{}^{80}Br$	0.03±0.01
$C_4H_7{}^{80}Br$	0.06±0.01

Composition of gases

c-C_5H_{10}	: 300 Torr
CF_3Br	: 30 Torr
$H_2S + O_2(2:3)$	: 40 Torr
Ar	: 30 Torr
Total pressure	: 400 Torr.

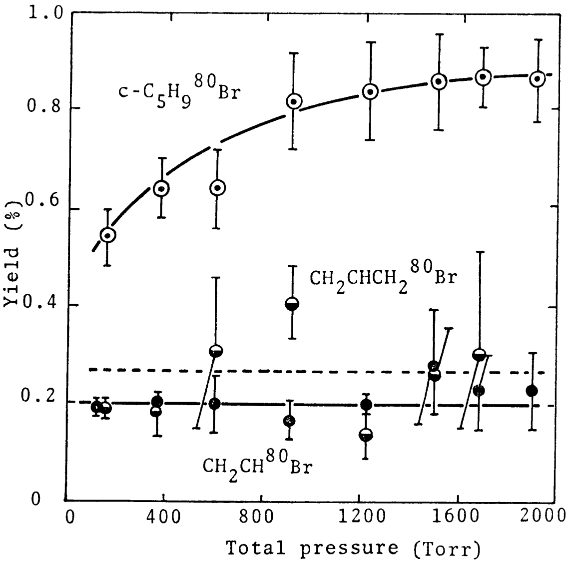

Fig. 2. Pressure-dependences of main products in c-C_5H_{10} system.
⊙: c-$C_5H_9{}^{80}Br$, ◒: $CH_2CHCH_2{}^{80}Br$, ●: $CH_2CH^{80}Br$.

to CH_3Br, on the basis of the fact that the change in the source molecule causes no significant difference in the results of the reaction of ^{80}Br from the (n, γ) process.[1)]

The major products were c-$C_6H_{11}{}^{80}Br$, $CH_2CH^{80}Br$, and $C_4H_7{}^{80}Br$[2)]; their relative yields were 1.0 : 06±0.2 : 0.6±0.2 at the system pressure of 120 Torr. Although $CH_3{}^{80}Br$ was also observed as a minor product, most of it resulted from the reaction of ^{80}Br with the source molecule. Thus, the quantitative determination of $CH_3{}^{80}Br$ from c-C_6H_{12} was not successful.

Discussion

Decomposition Pathways of Primary Products. When one considers the unimolecular decomposition of a primary product from a hot atom reaction, a knowledge of the decomposition mechanisms of the same compound in thermolysis and/or photolysis is very helpful. From the reported results,[3)–8)] the following decomposition pathways can be expected for the excited (c-C_4H_7-^{80}Br)* and (c-$C_5H_9{}^{80}Br$)*:

$$(c\text{-}C_4H_7{}^{80}Br)^* - \left| \begin{array}{lr} \xrightarrow{S} c\text{-}C_4H_7{}^{80}Br & (1) \\ \xrightarrow{D_1} CH_2CH^{80}Br + C_2H_4 & (2) \\ \xrightarrow{D_2} H^{80}Br + C_4H_6(\diagup\!\!-\!\!\diagdown) & (3) \end{array} \right.$$

$$(c\text{-}C_5H_9{}^{80}Br)^* - \left| \begin{array}{lr} \xrightarrow{S} c\text{-}C_5H_9{}^{80}Br & (4) \\ \xrightarrow{D_1} CH_2CH^{80}Br + C_3H_6 & \\ \quad \text{or } CH_2CHCH_2{}^{80}Br + C_2H_4 & (5) \\ \xrightarrow{D_2} H^{80}Br + c\text{-}C_5H_8 & (6) \end{array} \right.$$

Su *et al.* have studied the reactions of $^{80,82}Br$ from isomeric transitions with bromocyclobutane and cyclobutane.[9)] However, their experimental measurements were limited to only two systems, in the gaseous phase at 800 Torr and in the liquid phase. Furthermore, they used O_2 as a scavenger and added O_2 to the reaction system in order to constitute 4 mol% of the total pressure. According to the present results, however, 4% of O_2 is not enough to reduce the non-energetic processes down to the limits of experimental uncertainty. Thus, very possibly, their results are contaminated to a significant extent by the thermal reactions.

In Fig. 1, the yield of $CH_2CH^{80}Br$ in the absence of ethane is constant within the limits of experimental uncertainties, at least up to the pressure of 800 Torr. In the presence of ethane, the $CH_2CH^{80}Br$ must be corrected for its formation from ethane. The separate experiments show that the $C_2H_5{}^8$ Br/$CH_2CH^{80}Br$ ratio from ethane increases with the pressure from 6.9 at 100 Torr to 9.9 at 800 Torr. Above 800 Torr, this ratio stays constant at 9.9. Thus, the present correction is based on the assumption that these ratios are also maintained in the C_2H_6–c-C_4H_8 binary system. The corrected yield shows a broad maximum in the pressure range of 1000—2000 Torr. However, there is a tendency to decrease at pressures less than 1000 Torr, largely because of the uncertainty involved in the correction for the yield of $CH_2CH^{80}Br$ from ethane. Consequently, it can be considered that the yield of $CH_2CH^{80}Br$ is almost constant at pressures less than 2000 Torr, while above that point it seems to decrease slightly with the pressure.

On the other hand, the yield of c-$C_4H_7{}^{80}Br$ increases rapidly with an increase in the pressure at the beginning, followed by a gradual increase in the reaction systems both with and without ethane.

In the previous paper,[1)] a correlation was found between the excitation energy of a primary product and the dissociation energy of a reacting bond. From the correlation, the excitation energy of the primary product formed by the ^{80}Br-for-H reaction is estimated to be around 5 eV. (The authors express the excitation energy in units of eV throughout this paper, 1 eV= 96.49 kJ mol^{-1}.) If the (c-$C_4H_7{}^{80}Br$)* either decomposes through Reaction 2 or stabilizes collisionally as Reaction 1, the ratio of the decomposition product and the stabilized one is calculated by applying the Kassel theory.[10)] However, without any thermodynamic data for Reaction 2 available, we attempted to calculate the yield ratio using the values of A and E reported for c-C_4H_7Cl[3)] with a value for the classical oscillators, S, of either $1/2(3N-6)$ or $2/3(3N-6)$. In these calculations, where the correct values are not used, the calculated results do not always agree quantitatively with the experimental results, but they can furnish qualitative view of the features of the decomposition-stabilization processes. The results obtained, however, are far from explaining the results shown in Fig. 1. This suggests the existence of decomposition processes other than Reaction 2.

On the thermolysis of c-C_4H_7Cl, Cocks and Frey reported that the activation energy of Reaction 7 was higher than that of Reaction 8:[3)]

$$c\text{-}C_4H_7Cl - \left| \begin{array}{lr} \longrightarrow CH_2CH_2 + CH_2CHCl & (7) \\ \quad E_a = 60.07 \pm 0.30 \text{ kcal mol}^{-1} & \\ \longrightarrow C_4H_6(\diagup\!\!-\!\!\diagdown) + HCl & (8) \\ \quad E_a = 55.24 \pm 0.19 \text{ kcal mol}^{-1} & \\ \quad (1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}) & \end{array} \right.$$

They also investigated the pyrolysis of *t*-butylcyclobutane and reached the conclusion that this substrate is decomposed to ethylene and 3,3-dimethyl-1-butene.[7] Thomas *et al.* reported, in connection with thermal decomposition of methylcyclobutene, that the principal products were ethylene and propylene, and that the isomerization to 1-pentene accounted for 0.5—1.8% of the reaction.[6]

In the present case, therefore, the ring-opening reactions of the excited (c-$C_4H_7{}^{80}Br$)* to $C_4H_7{}^{80}Br$'s are not an important decomposition process. This consistent with the fact that the $C_4H_7{}^{80}Br$ yield has a positive dependence on the pressure. This means that the $C_4H_7{}^{80}Br$ is not a decomposition product of the excited (c-$C_4H_7{}^{80}Br$)*, but, rather, a primary product resulting from an attack of the incident ^{80}Br on a C–C bond:

$$^{80}Br^* + c\text{-}C_4H_8 \rightarrow (C_4H_7{}^{80}Br)^*[\text{Bromobutene}] \qquad (9)$$

Thus, the main decomposition process of (c-$C_4H_7{}^{80}Br$)* are limited in Reaction 2 or 3. No definite conclusion can be drawn as to the relative importances of these decomposition processes without adequate thermodynamic data. However, by analogy with the case of c-C_4H_7Cl, it is considered that the activation energy of Reaction 3 is lower than that of Reaction 2. Thus, a plausible explanation for the present results is as follows: the excited products formed by the ^{80}Br-for-H reaction with c-C_4H_8 decompose competitively through Reactions 2 and 3. Reaction 3 predominantly occurs with less excited primary products and is easily suppressed by an increase in the pressure. The decomposition mode of Reaction 2 giving $CH_2CH^{80}Br$ occurs with highly excited products and can only be suppressed at pressures above 2000 Torr.

As is shown in Table 2, the spectrum of the reaction products in the c-C_5H_{10} system is more simple than that in the c-C_4H_8 system. There exists no organic product to compensate for the increase in the yield of c-$C_5H_9{}^{80}Br$ with an increase in the pressure. Thus, by analogy with the case of c-C_4H_8, it can be deduced, as for the decomposition processes of the excited (c-$C_5H_9{}^{80}Br$)*, that they decompose through Reaction 5 or 6, and that Reaction 6 occurs significantly on the lower-pressure side, as can easily be understood from Fig. 2. One support for this consideration comes from the fact that the main decomposition pathway in the pyrolysis of c-C_5H_9Br is Reaction 6.[4,5]

Even though the activation energy of Reaction 11 is slightly higher than that of Reaction 6,[11] the HBr-elimination-mode may still play a rather important role in the decomposition of the excited (c-$C_6H_{11}{}^{80}Br$)*. The yields of $CH_2CH^{80}Br$ and $C_4H_7{}^{80}Br$, relative to c-$C_6H_{11}{}^{80}Br$, are high; thus, Reaction 12 must be another decomposition pathway:

$$(c\text{-}C_6H_{11}{}^{80}Br)^* - \begin{array}{ll} \xrightarrow{S} c\text{-}C_6H_{11}{}^{80}Br & (10) \\ \xrightarrow{D_1} H^{80}Br + c\text{-}C_6H_{10} & (11) \\ \xrightarrow{D_2} CH_2CH^{80}Br + C_4H_8 & \\ \quad \text{or } C_4H_7{}^{80}Br + C_2H_4 & (12) \end{array}$$

The excitation energy of a primary product from a hot atom reaction spreads over an extremely wide range.[12] Thus, it can be thought that $CH_2CH^{80}Br$ in the c-C_4H_8 system, $CH_2CH^{80}Br$ and $CH_2CHCH_2{}^{80}Br$ in the c-C_5H_{10} system, $CH_2CH^{80}Br$ and $C_4H_7{}^{80}Br$ in the c-C_6H_{12} system are decomposition products from highly excited primary products. However, the greater part of the primary products is not excited enough to cleave the ring and will release $H^{80}Br$ or stabilize in collision with other molecules. However, in the present systems, no products with a negative pressure dependence were found in the pressure range studied. Thus, the experimental justification of the above consideration must rely on the measurement of $H^{80}Br$ as a function of the pressure, this has not yet suceeded.

Systematics of Total Organic Yield. It is very interesting and worth while to study the systematics in the reaction of a hot atom with various reactants in order to obtain more information about the hot atom reaction. Thus far, a number of systematic studies have been reported for the reaction of hot tritium. Rowland *et al.* have found that the yields of the tritiated alkanes and haloalkanes formed by the T-for-H reaction have a linear relationship with the NMR proton chemical shift.[13] On the other hand, Williams *et al.* have reported that the yields of CH_3T from the hot tritium abstraction of end methyl groups show no obvious effect on the electron density around the reaction site, but are correlated inversely with the R–CH_3 bond dissociation energy.[14]

Such discussions as have been given as examples must be based on the yield of a primary product. Unfortunately, in the present reaction system, it is rather difficult to estimate the primary yields from the ^{80}Br-for-H reactions, since not all the decomposition products can be determined experimentally, as was mentioned in the preceding section. Thus, the total organic yields found at the higher system pressure are chosen as the second-best values.

Table 3 shows the total organic yields obtained at two different system pressures, 600 and 1600 Torr, along with the experimental conditions. An excess portion of ethane which was added as a pressure-builder to the reaction system also served as a kinetic moderator to obtain identical kinetic spectra of the recoil ^{80}Br for all samples. For the c-C_6H_{12} system, the experiment at 1600 Torr cannot be performed simply because the vapor pressure of c-C_6H_{12} is much less than 400 Torr.

TABLE 3. TOTAL ORGANIC YIELDS AT SYSTEM PRESSURES OF 600 AND 1600 Torr

Reactant	Total organic yield		Ratio
	600 Torr[a)]	1600 Torr[b)]	
c-C_3H_6	1.7±0.3%	2.8±0.1%	1.7±0.3
c-C_4H_8	1.4±0.2	2.5±0.3	1.8±0.3
c-C_5H_{10}	1.3±0.2	1.9±0.2	1.5±0.3
c-C_6H_{12}	1.0±0.1	···	···

Composition of gases	a)	b)
Reactant	100 Torr	400 Torr
CH_3Br	10 Torr	10 Torr
$H_2S + O_2$ (2 : 3)	60 Torr	160 Torr
C_2H_6	430 Torr	1030 Torr

As may be seen in Figs. 1 and 2, at around 600 Torr the yields of the parent products are very sensitive to, and increase with, the pressure. However, the yields at the pressure of 1600 Torr are very close to the plateau values. In all cases, the ratio of the total organic yields obtained at these two different pressures stays almost constant within the limits of experimental uncertainty, as is shown in the last column of Table 3. This means that, in a qualitative sense, the excitation energies of these primary products are in a similar range. Thus, their decomposition is equally suppressed by increasing the pressure.

Consequently, the results shown in Table 3 can be compared with each other without any further adjustment. In the present case, the yields show no clear correlation with either the dissociation energy of a C–H bond[15,16] or the electron density around the hydrogen replaced.[17] On the other hand, the plots of the yields against the strain energy of the ring[18] seem to show a certain correlation; the yields decrease with the strain energy. If the total organic yield is correlated directly with the probability of the ring-opening reaction, as in Reaction 9, the most believable explanation for this results will be as follows: when the substrate is attacked by an energetic ^{80}Br, the possibility of the ring-cleavage is inversely proportional to the strain energy of the ring. Thus, a higher organic yield results from the substrate having a higher strain energy. However, it has already been confirmed that the ring-opening reaction plays a minor role in the reaction of hot atoms with cyclanes.[1,12] This is also the case in the present systems, as has already been discussed in the preceding section. Thus, all the features of the experimental results can not be interpreted only in terms of the strain of the ring.

When the total organic yields were plotted against the number of carbon atoms, a linear relationship was obtained; the yields decreased with the carbon numbers, as is shown in Fig. 3. A similar trend is also noticed in the reactions of ^{80}Br with simple alkanes;[19–24] the yields of the products resulting from the ^{80}Br-for-H reactions decrease with the carbon numbers, as is also shown in Fig. 3 as a reference. In these cases, however, the trend is not clearly seen in the total organic yields simply because, in the reactions with alkanes, the yields of the products from the ^{80}Br-for-(alkyl group) reactions constitute a greater part of the total organic yields.

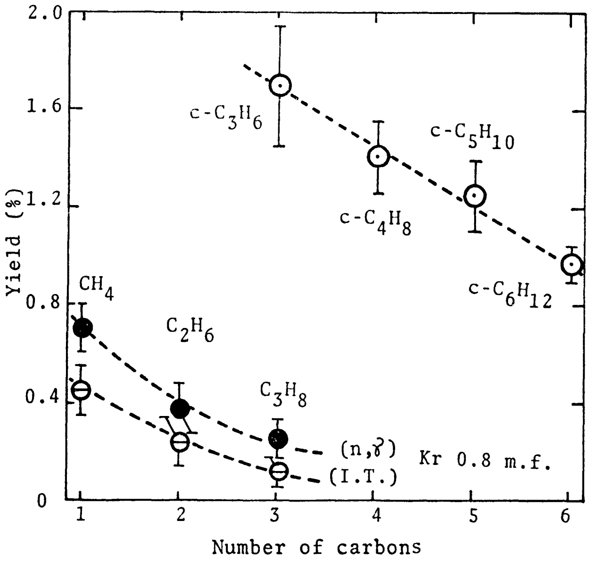

Fig. 3. Correlations between total organic yield and carbon-numbers.
⊙: Cyclane + ^{79}Br(n, γ)^{80}Br, (moderator; ethane, total pressure; 600 Torr).
●: Alkane + ^{79}Br(n, γ)^{80}Br, (moderator; Kr, total pressure; 700 Torr).
⊖: Alkane + ^{80m}Br(I.T.)^{80}Br, (moderator; Kr, total pressure; 700 Torr).

There seem to exist several factors consistent with the present findings. Among them, the most conceivable ones are: 1) the elimination of H^{80}Br as a decomposition process of the primary products, 2) the competition between the abstraction and substitution reactions in the primary reactions of ^{80}Br with a reactant molecule, and 3) the inherently possessed reaction probability of cyclanes toward the recoil ^{80}Br. The first factor will be ignored because of the following consideration. The elimination of H^{80}Br as a decomposition process of the excited product is important only in the lower-pressure end and will be essentially suppressed at the pressure of 1600 Torr. As for the second determinant, by analogy with the reaction of recoil T,[25,26] the ^{80}Br-to-H^{80}Br reaction may also be sensitive to the C–H bond strength. All the reactants chosen in the present work except c-C_3H_6 have a C–H bond strength in the range from 93 to 95 kcal mol^{-1}. This small variation in the bond energy is rather far from the explanation of the above correlation, suggesting the insignificance of the second factor.

Thus, with reasonably confidence, the relationship may be explained in connection with the reaction probability itself; the probability decreases with an increase in the carbon numbers. As the complexity of a molecule increases, the vibration modes available also increase. As a result, the life of a intermediate complex[27,28] will become longer, because the internal excitation energy spreads over the bonds involved. In these circumstances, the probability of the rupture of any particular bond rapidly decreases with an increase in its bond strength. In the present cases, the C–Br bond in the intermediate complex will have the weakest energy and will be broken with a high probability, ejecting the incident ^{80}Br with a reduced energy. This explanation is also consistent with the following consideration.

In the reaction of recoil T with cyclanes,[29,30] the yields of the parent products seem to stay within a certain range or seem to increase very slightly with the carbon numbers. This observation may be understood as follows: the difference in the bond energy between the C–H and C–T is very small, and the relative probability of the rupture of these bonds in the intermediate complex will hardly be influenced at all by the life of the complex.

Thus, it can be concluded that the life of the intermediate complex may play a more important role than the strain energy of the ring in the reaction of ^{80}Br with cyclanes.

Appendix

Product-Distribution and Radiolysis. As is shown in Tables 1 and 2, the numbers of the products are 8 for the c-C_4H_8 system and 6 for the c-C_5H_{10} system. In the c-C_6H_{12} system, this decreases to only 4. This tendency seems somewhat strange, because it is the opposite of the increase in the carbon numbers of the reacting substrate.

In the radiolysis of cyclanes, the G values of H_2 increase with the number of carbons. However, those of hydrocarbons, especially those resulting from the cleavage of the ring, decrease with an increase in stability of the ring.[31,23] Thus, in the present case, the variation in the number of the products from different cyclanes will be considered in connection with the stability of the reactant in radiolysis.

As was described in the chapter on "Results", the products from the c-C_4H_8 system were divided into two groups, scavenger-sensitive and scavenger-insensitive. The products belonging to the former group may originate from the radiolysis of the parent molecule, because they have no pressure dependence and always have low yields, particularly in highly scavenged systems.

In the experiments on c-C_4H_8 scavenged by Br_2, some polybromoalkanes which have a smaller carbon-skeleton than C_4 were formed. These products also resulted from the reaction of the fragments from the radiolysis. The $CH_2BrCH_2{}^{80}Br$ can be chosen as a typical example among these products. This product shows a steep scavenger curve at the beginning of the Br_2 concentration. In the system of 2% Br_2, the yield of $CH_2BrCH_2{}^{80}Br$ increased linearly with the irradiation period. This may be explained according to the following reactions initiated by the radiolysis of c-C_4H_8:

$$c\text{-}C_4H_8 \xrightarrow{\gamma} \cdot CH_2CH_2CH_2\dot{C}H_2 \qquad (13)$$

$$\cdot CH_2CH_2CH_2\dot{C}H_2 \xrightarrow{Br_2} \cdot CH_2CH_2CH_2CH_2Br \qquad (14)$$

$$\cdot CH_2CH_2CH_2CH_2Br \longrightarrow \cdot CH_2CH_2Br + C_2H_4 \qquad (15)$$

$$\cdot CH_2CH_2Br \xrightarrow{Br_2} CH_2BrCH_2Br \qquad (16)$$

The butylene biradical formed by Reaction 13 may decompose to $\cdot CH_2\dot{C}H_2$ or ethylene. However, Horváth *et al.* have reported that the G value of C_4 products from c-C_4H_8 is about 2 times higher than that of C_2 products.[31] Thus, $CH_2BrCH_2{}^{80}Br$ should be chiefly formed through Reactions 13—16.

If we use Br_2 as a scavenger in the reaction with a substrate having a lower radiation-resistance, its radiolysis will, sometimes, make a hot atom reaction complex. In such cases, it is advisable to chose another reagent, such as H_2S or a mixture of H_2S and O_2, as a scavenger, because H_2S will allow the radicals from radiolysis to convert saturated hydrocarbons by abstracting the H-atom.

In the present case, a mixture of H_2S and O_2 was used as the scavenger and the irradiation length of the sample was limited as short as possible. Thus, it is certain that the contribution of radiolysis to the data dealt with in this paper is not significant.

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