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# Isotope Effects in the Reactions of $^{80}$Br Activated by Isomeric Transition with Various Deuterated Propanes

Enzo Tachikawa and Kenshi Numakura
*Division of Chemistry, Japan Atomic Energy Research Institute, Tokai-Mura, Ibaraki 319-11*

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Product studies of the reactions of recoil $^{80}$Br with propanes in binary mixtures with ethane showed that the difference in the energy-loss efficiency of $C_3H_8$ and $C_3D_8$ in collision with $^{80}$Br was less than 10%. Then, the yields for the substitution of $^{80}$Br for atoms or groups have been compared in various deuterated propanes. A reactivity integral-isotope effect has been observed in the yields of products from $CD_3CD_2CD_3$ and $CD_3CH_2CD_3$, except in the case of isopropyl bromide from the latter compound. However, it has been observed only in the yield of iso propyl bromide from $CH_3CD_2CH_3$. These results indicate that the chemical and physical properties of both replaced and residual atoms or groups play a role in the observed isotope effects. With a "complex" formation mechanism, it is suggested that an isotope effect appears mostly when the kinetic energy of the reacting $^{80}$Br is at the lower-energy end of the reaction-energy range.

One of the experimental approaches used to obtain valuable information concerning the mechanisms and characteristics of the reactions of energetic atoms is to measure the isotopic variation in the reaction yields from protonated and deuterated reactants. Thus far, the existence of the isotopic preference in the substitution reaction of $^{80}$Br for H over D has been demonstrated in $CH_4$–$CD_4$[1,2] $C_2H_6$–$C_2D_6$[3] and $CH_3F$–$CD_3F$[4] systems. However, these observed reactivity integral-isotope effects directly reflect the composite of the primary and secondary isotope effects. The relative importance of the magnitude of these effects can be evaluated through competitive experiments in the intra- and inter-molecular comparisons of various deuterated compounds.

The present paper will deal with the isotopic variation between $C_3H_8$ and fully- or partially-deuterated propanes in the substitution reaction of the $^{80}$Br activated by the isomeric transition. The results obtained cannot be explained solely by the two models so far proposed for the substitution reaction of the recoil tritium atoms; one of them based on the rotational inertia,[6,7] and the other, on the electronegativity[8–10] of the residual group. Instead, the results indicate that a complete explanation must involve an effect combining the physical and chemical properties of the replaced atom or group, and those of the residual group.

## Experimental

*Sample Preparation and Analysis.* The preparation of samples followed the routine procedures used in our previous work for gas-phase bromine hot atom chemistry.[11] The $^{80m}$Br$^{}$Br was formed by irradiating gaseous $Br_2$ with thermal neutrons for one minute in a JRR-4 reactor at JAERI. The reaction mixture was allowed to stand more than 2 hr to permit a $^{80m}$Br$^{80}$Br parent-daughter equilibium to be established. All the samples contained 65 Torr of oxygen in order to exclude the formation of isopropyl bromide tagged with $^{80}$Br by light- or radiation-induced reaction. The total pressure was always kept constant at 710±10 Torr. The reaction products were analyzed by means of a radio-gas chromatograph equipped with a flow-type G-M counter. The results obtained were processed using the BOB 7 series program[12] corrected for the background and for the radioactivity decay of nuclides.

*Percentage Yield.* The less than 0.1% of propylene present as an impurity in propane significantly interfered with the direct measurement of the total organic yield.[11] Thus, the absolute yield has been measured only from the $^{80}$Br–$C_2H_6$–$O_2$ (3.2±0.1%) system by a solvent-extraction method. Individual radioactivity yields have been obtained by dividing the activities in the radio-gas chromatogram by the total $^{80}$Br activity, as measured with a G-M counter 2 hr after sampling the gases. The relative yields have been normalized to the percentage yields using a conversion factor determined from the sum of the relative yields and from the total organic yield found in the above system. The chief uncertainty involved in this procedure is introduced in the measurement of the total $^{80}$Br activity, and the accuracy in the percentage yield obtained is usually limited to ±10%.

*Chemicals.* Ethane and $C_3H_8$ of the highest grade were obtained from the Takachiho Chemical Co. The deuterated propanes came from the Merk Sharp and Dohme Co., their listed purities were all 98%. These reagents were used after the freezing-thawing purification had been repeated several times.

## Results and Discussion

Bromine-80 activated from the (I.T.) process reacts with hydrocarbons either by an energetic process or by a non-energetic process; the relative importance of the latter depends on the circumstances.

The most common means of identifying energetic reactions is the addition of a chemically-inert moderator to the system. In general, noble gases are used as moderators. Such moderators have no effect on the thermal energy distribution. However, by reducing the excess kinetic energy of an energetic atom in each collision, the moderator will reduce and sometimes eliminate energetic reactions.

Of particular importance is the early recognition that the charge state of the reacting $^{80}$Br is primarily controlled by the ionization potential of the constituents of the reaction systems, and that an additional product is formed *via* thermal ionic processes in the presence of an inert gas with a higher ionization potential than that of Br. Thus, the reactions in the binary system have been studied using $C_2H_6$ as a counterpart as in the previous paper.

Table 1 shows the yield variation in the products in

Table 1. Percent $^{80}Br$ stabilized in organic combination in $C_3D_8$–$C_2H_6$ binary system[a]

| $\frac{C_3D_8}{C_3D_8+C_2H_2}$ | Methy bromide (%) | Ethyl bromide (%) | *i*-Propyl bromide (%) | *n*-Propyl bromide (%) | Methylene bromide (%) |
|---|---|---|---|---|---|
| 1.00 | 0.77±0.02 | 0.36±0.02 | 0.15±0.02 | 0.49±0.03 | 0.30±0.03 |
| 0.801 | 0.90±0.02 | 0.50±0.02 | 0.13±0.02 | 0.44±0.02 | 0.33±0.03 |
| 0.545 | 1.10±0.02 | 0.69±0.08 | 0.09±0.01 | 0.35±0.02 | 0.39±0.02 |
| 0.287 | 1.25±0.02 | 0.93±0.02 | 0.05±0.01 | 0.20±0.01 | 0.42±0.01 |
| 0.054 | 1.62±0.02 | 1.18±0.02 | — | 0.06±0.01 | 0.53±0.01 |
| 0.00 | 1.53±0.02 | 1.23±0.02 | — | — | 0.40±0.02 |

a) Average of several measurements

$C_3D_8$–$C_2H_6$ mixtures, the m.f. of the latter varying from zero to 1.0. With the addition of $C_2H_6$, the yields of iso- and *n*-propyl bromides, which are formed only from $C_3D_8$, decrease from 0.15±0.02 and 0.49±0.03 respectively to zero. However, methyl, ethyl, and methylene bromides are formed from the reactions with either constituent; the observed yields are the sum of those from both constituents. The contribution to the overall observed yield from each constituent can be estimated on the assumption that the relative yield distribution among the products from $C_3D_8$ remains constant over the entire range of the m.f. of $C_3D_8$. This permits the calculation of the yields of products at any m.f. of $C_3D_8$ by simply multiplying the percentage yield of *n*-propyl bromide by the constant determined based on the yields found without the addition of $C_2H_6$.

The corresponding yields of products originating from $C_2H_6$ can be obtained as the difference between the calculated yield and the observed yield at any measuring point; the yields are shown in Fig. 1. The results show that the yield decreases to zero with an increase in the m.f. of $C_3D_8$ and that no significant interference of other possible processes exists in the yield variation. This implies that the thermal ionic process is not important in this binary system as the case in the $C_3H_8$–$C_2H_6$ system.[11]

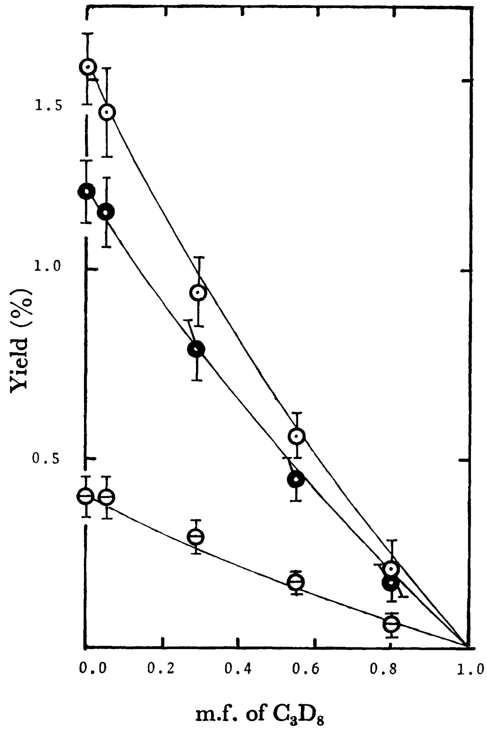

Fig. 1. Estimated and Calculated Yields of Products in Reactions of $^{80}Br$ with $C_2H_6$
Estimated yield; ⊙: methyl bromide ●: ethyl bromide, ⊖: methylene bromide, Calculated yield; solid line (equation 1)

The solid lines are the yield curves obtained using this equation;[11]

$$\frac{1}{P}=\frac{\alpha_{(C_3D_8)}}{I}+\frac{\alpha_{(C_2H_6)}}{I}\cdot\frac{f_{(C_3D_8)}+A\cdot f_{(O_2)}}{f_{(C_2H_6)}} \qquad (1)$$

where $A=\alpha_{(O_2)}/\alpha_{(C_3D_8)}$. The $f_i$ is the relative probability of the collision of $^{80}Br$ with the i component, and where $\alpha_i$ is the average energy loss on collision with the i component. For the calculation, $\alpha_{(C_3D_8)}/\alpha_{(C_2H_6)}$ was equalized to $\alpha_{(C_3D_8)}/\alpha_{(C_2H_6)}$, which had previously been determined as 1.1 with $A$=0.65 in the $^{80}Br$–$C_3H_8$–$C_2H_6$–$O_2$ system.[11] The fit of the estimated values on the calculated curve is reasonably good, but at the higher m.f. values of $C_3D_8$ the deviation becomes large and amounts to roughly 10%. In the present calculation, a little uncertainty in the yield from the major constituent leads to a large uncertainty in the yield from the counterpart; a 10% uncertainty in the former causes roughly 20—30% uncertainty in the latter, which covers the observed deviation in Fig. 1. Thus, the deviation from the solid lines toward the lower yield results mostly from the uncertainty in the yield from $C_3D_8$, but partly from the moderator-isotope effect[5] between $C_3D_8$ and $C_3H_8$. The moderator-isotope effect introduced by replacing H in $C_3H_8$ by D must be largest between $C_3H_8$ and $C_3D_8$, since these are the two extreme compounds. Thus, as for the present analysis, the moderator-isotope effect is considered to be less than 10%. This allows us to compare the yields of products from various deuterated propanes without correction for any difference in the moderating efficiency of these compounds within this limited accuracy.

*Reactivity Integral Isotope Effect.* Table 2 summarizes the product yields from various deuterated propanes. The *K* values in the table are the yields from fully protomated propane, relative to that from deuterated propane, and are equal to an overall isotope effect in the formation of the products under given conditions.

These results require essentially no correction for the kinetic energy-independent processes of the $^{80}Br$ atom.

Table 2. Yields of products formed by reactions of $^{80}$Br with variously deuterated propanes

| Products | Reactant | | | | | | |
|---|---|---|---|---|---|---|---|
| | $CH_3CH_2CH_3$ (%) | $CH_3CD_2CH_3$ | | $CD_3CH_2CD_3$ | | $CD_3CD_2CD_3$ | |
| | | (%) | $(K)$[a] | (%) | $(K)$[a] | (%) | $(K)$[a] |
| Methyl bromide | 1.12±0.11 | 1.05±0.11 | (1.1) | 0.82±0.08 | (1.4) | 0.77±0.08 | (1.5) |
| Ethyl bromide | 0.57±0.06 | 0.54±0.05 | (1.1) | 0.38±0.04 | (1.5) | 0.36±0.04 | (1.6) |
| *i*-Propyl bromide | 0.20±0.02 | 0.15±0.02 | (1.3) | 0.19±0.02 | (1.1) | 0.14±0.01 | (1.4) |
| *n*-Propyl bromide | 0.67±0.07 | 0.60±0.06 | (1.1) | 0.45±0.05 | (1.5) | 0.49±0.05 | (1.4) |
| Methylene bromide | 0.47±0.05 | 0.50±0.05 | (0.94) | 0.35±0.04 | (1.3) | 0.30±0.03 | (1.6) |
| Total | 3.03 | 2.84 | | 2.19 | | 2.06 | |

a) $K=\dfrac{\text{Product yield from } CH_3CH_2CH_3}{\text{Product yield from deuterated propane}}$ .

In order to make an intermolecular comparison of the product yield, however, the results must be corrected for both the secondary decomposition of the excited primary products[13–15] and the non-equivalence of the $^{80}$Br spectrum in each sample.[1,16]

Such unimolecular decomposition processes can be conveniently investigated by pressure-variation experiments, such as were previously carried out with $C_3H_8$.[11] In the pressure range between 600 to 1600 Torr, the yields of products remained almost constant, and the intermolecular distribution of the $^{80}$Br atom among the products was essentially constant. Thus, without further quantitative knowledge concerning the decomposition products, it can only be assumed that a direct comparison of the yields of the individual products requires no significant correction for the secondary decomposition. This is a reasonable assumption since, if such a decomposition occurs, its extent will be as large or greater in protonated than in deuterated compounds. This is the reverse of the isotope effect observed, and any correction for the decomposition tends to further enlarge the isotope effect.

For the second correction for the $^{80}$Br atom flux, we need correct knowledge concerning the energy-loss processes of energetic $^{80}$Br atoms. However, experimentally, the $^{80}$Br atom flux can be controlled by the addition of a large excess of a common molecule as an energy moderator.[16] Table 3 shows the yields of the iso- and *n*-propyl bromides found in the presence of 0.5 m.f. of $C_2H_6$. The results show a similar trend as in the absence of $C_2H_6$, a preference for the substitution of H over D atoms.

These results, together with those in Fig. 1 make it reasonably sure that the $K$ values in Table 1 are a good measure of the isotopic variation in the reactivities of various deuterated propanes toward the energetic $^{80}$Br atoms.

*$^{80}$Br-for-R Reaction.* One of the things shown in Table 1 is that the isotope effect on methyl, ethyl, and methylene bromides appears on both $C_3H_2D_6$ and $C_3D_8$, but not on $C_3H_6D_2$. These results are not fully predicted either by the rotational inertia effect of the residual group[6] or by the electronegativity[9,10] of the replaced atom or group. The former can predict only an isotope effect on methyl bromide, and the latter essentially no isotope effect.

The absence of the isotope effect on the methyl bromide yield from $C_3H_6D_2$ indicates practically no effect of the D atom in the methylene group on the $^{80}$Br-for-ethyl reaction. Thus, the isotope effect on the $^{80}$Br-for-ethyl reaction in both $C_3H_2D_6$ and $C_3D_8$ must originate from the replacement of H by D in the residual methyl group or from that in the methyl in the ethyl group. However, any effect of the D atom separated by C–C bond on the reactivity is generally much less important than that of the D atom attached to the reacting C atom; the observed isotope effect results from the difference in the chemical and physical relaxation of the residual $CH_3$ and $CD_3$ groups.

A similar consideration suggests that any consistent explanation for the isotope effect on the ethyl bromide must involve a quick rearrangement of the replaced methyl group for a stable combination between the $^{80}$Br atom and the residual ethyl group. These facts indicate that a complete explanation of the isotope effect must be based on the properties of the residual as well as the replaced atom or group.

In the formation of methylene bromide, there are two possible reaction processes; one is the double replacement[17,18] of the H atom and the ethyl group (Reaction 2), while the other is the replacement of two methyl groups (Reaction 3):

$$CH_3CH_2CH_3 + {}^{80}Br \longrightarrow CH_2{}^{80}Br + H + CH_3CH_2 \quad (2)$$

$$CH_3CH_2CH_3 + {}^{80}Br \longrightarrow CH_2{}^{80}Br + 2CH_3 \quad (3)$$

$$CH_2{}^{80}Br + Br_2 \longrightarrow CH_2{}^{80}BrBr + Br \quad (4)$$

Table 3. Yields of *i*- and *n*-propyl bromides in presence of 0.5 m.f. of $C_2H_6$

| Products | Reactant | | | | | | |
|---|---|---|---|---|---|---|---|
| | $CH_3CH_2CH_3$ (%) | $CH_3CD_2CH_3$ | | $CD_3CH_2CD_3$ | | $CD_3CD_2CD_3$ | |
| | | (%) | $(K)$ | (%) | $(K)$ | (%) | $(K)$ |
| *i*-Propyl bromide | 0.14±0.01 | 0.10±0.01 | (1.4) | 0.13±0.01 | (1.1) | 0.10±0.01 | (1.4) |
| *n*-Propyl bromide | 0.43±0.04 | 0.40±0.04 | (1.1) | 0.31±0.03 | (1.4) | 0.33±0.03 | (1.3) |

In the former case, the isotopic preference of the substitution of H over D is the origin of the observed isotope effect, while in the latter the rapidity of the adjustment of the two leaving methyl groups to the formation of $CH_2{}^{80}Br$ is the determining factor. At present, no definite conclusion can be drawn. However, the former process seems much more probable than the other, since, in the latter process, both methyl groups can influence the probability of the combination of the resulting methylene with $^{80}Br$ and an isotope effect nearly twice as large as the observed one can be expected.

*$^{80}$Br-for-H Reaction.* Both iso- and *n*-propyl bromides are formed by the $^{80}$Br-for-H reaction. In this type of reaction, three kinds of isotope effects resulting from the replacement of H by D in the molecule can be considered. The first kind is the primary isotope effect, an isotopic preference for the substitution of H over D. The second is a secondary isotope effect of D atom attached to the reacting C atom; it is accounted for by the ease of the adjustment for the subsequent stable combination with the $^{80}$Br atom with the C-atom. The third is also termed as a secondary isotope effect, but, in this case, the D atom is separated by the C–C bond from the reacting C-atom.

The absence of the isotope effect in the yields of isopropyl bromide from $C_3H_2D_6$ and of *n*-propyl bromide from $C_3H_6D_2$ indicates that the D atom in the methyl group in propane has no measurable effect on the $^{80}$Br-for-H reaction in the methylene group, while the D atom in the methylene group has no measurable effect on the reaction in the methyl group. This indicates the absence of the third kind of isotope effect described above.

The first and second kinds of isotope effects cannot be readily distinguished in the present comparison. In principle, an obvious experiment to separate these two possibilities is the measurement of the isopropyl bromide yield from $C_3HD_7$. However, according to the concept of the inertia model, the second kind of isotope effect is less important when an atom or group larger than a H atom is attached to the same C atom. Thus, the observed isotope effect in the $^{80}$Br-for-H reaction may be ascribed principally to the primary isotope effect of the replaced D atom.

When we compare the present isotopic variation in the substitution of H and D with the value of $1.6\pm0.2$ found with the $C_2H_6$–$C_2D_6$ pair,[3] a reasonable agreement can be seen.[4] However, those values are much smaller than the value, $2.7\pm0.3$, found with the $CH_4$–$CD_4$ pair.[1,2] The only logical explanation of this is that the secondary isotope effect originating from the D atom combined with the reacting C atom is important in methane, but less important in ethane and propane, since in the latter compounds the relaxation of the residual group is essentially controlled by that of the methyl or ethyl group attached to the reacting C atom. This means that the primary isotope effect in the substitution of H(D) can be assigned for a level of $1.4\pm0.2$, and that the large isotope effect in the $CH_4$–$CD_4$ pair results from the effect combining the primary and secondary isotope effects.

*Origins of Reactivity Integral Isotope Effect.* In Table 1 it is obvious that the total organic yield decreases with the number of D atoms in the reactant. A similar trend can also be noticed in the reaction of recoil T with various reactant molecules.[5] These results indicate that the total reactivity integral decreases with the deuteration of the reactant, within an allowance of less than 10% for the moderator isotope effect and with an almost constant extent of unimolecular decomposition of various deuterated products.

When the energetic atom strikes the atoms of a reactant molecule, much of its kinetic energy is transferred into the internal energy of the struck molecule. The atom is, then, imbedded in the electron distribution of the struck molecule and forms a "complex" of a short but still sufficiently long enough lifetime for reasonably normal isotope effects on decomposition to take effect.[5,19] However, it is noticed that the substitution reaction of $^{80}$Br for H leaves the resulting products, $R^{80}Br$, with the excitation energy spread over a wide energy range; the average value is estimated to be ~4 eV for RH=cyclopropane.[20]

It is rather unrealistic for a "complex" with such a high excitational energy to show an isotopic preference in its decomposition to the extent observed. One consistent explanation is that the isotope effect in the reaction of $^{80}$Br appears mostly when the kinetic energy of the atom is in the lower-energy end of the reaction-energy zone.[21] In these cases, the excess energy of the resulting "complex" is relatively small, and its subsequent decomposition is very sensitive to the properties of the atoms and groups involved. If the formation rates of a "complex" are assumed to be approximately equal for protonated and deuterated molecules, relatively more C–$^{80}$Br interaction will be ruptured in the latter and the $^{80}$Br will emerge very much degraded in energy. This is equivalent to the fact that the reaction probability in a collision of $^{80}$Br with $C_3D_8$ is smaller than in one with $C_3H_8$ at the lower-energy end of the reaction zone.

Although it has not been confirmed that the same explanation can be applied to the reaction of energetic tritium atoms, this is quantitatively consistent with a trend found in the latter system.[21] The 2.8 eV T atom resulting from the photolysis of TBr shows a much larger isotope effect than does the recoil T atom.[19]

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