Energetic Reactions of ^{80}Br Activated by (I. T.) Process in C_3H_8-C_2H_6 and C_3H_8-CH_3Br Systems

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In order to examine the relative importance of the thermal ionic process in the reactions of ^{80}Br from the (I. T.) process with C_3H_8, we chose C_2H_6 or CH_3Br as diluents. Some assumptions have made in estimating the yield-variation of products from the diluents: 1) the rate of the reduction of the yields of the products from C_3H_8 caused by the addition of the diluent is the same for all of the products and 2) the ionic yield is zero over the whole range of concentrations of C_3H_8. With these assumptions, the analysis of the results shows that the contribution of the thermal ionic process in these binary systems has only minor importance; the products are, essentially, formed *via* energetic processes. It is also found that the ratio of n-$C_3H_7{}^{80}Br/i$-$C_3H_7{}^{80}Br$ per bond basis seems to decrease from 1.1 ± 0.1 on the addition of the diluent. This indicates that the formation of i-$C_3H_7{}^{80}Br$ is a lower energy process, relative to that of n-$C_3H_7{}^{80}Br$ in the present reaction system.

In recoil ^{80}Br chemistry, the method commonly used to distinguish excess kinetic energy processes from others consists of the addition to the reaction system of an inert gas as a kinetic-energy moderator.[1-6] However, when a reactant molecule is diluted with an inert gas having a higher ionization potential (IP) than that of Br, the charge distribution, and the energy distribution of ^{80}Br are both influenced. Thus, the moderator curve obtained must be carefully analyzed in order to ascertain the real nature of the reactions involved. For example, the limiting yield at 1.0 m. f. of a moderator simply means that the yield is due to the thermal processes in the moderactor atmosphere and does not necessarily indicate the thermal yield in the reactant atmosphere.

In the previous paper we examined the nature of the reacting ^{80}Br activated by the isomeric transition in ethane,[6] which has a lower IP than that of Br, and speculated about it principally as a kinetically-excited atom, probably with on charge, on the basis of the assumption that the isotopic variation in the products is significant only when the products are formed *via* energetic processes.

The present paper will deal with the reactions of ^{80}Br with C_3H_8 in the binary system; C_2H_6 and CH_3Br were chosen as counterparts. All of these molecules have lower IP values than that of Br. Thus we can expect that the thermal ionic processes of ^{80}Br are not important in these systems if the above speculations are generally true. The conclusion drawn from the present results is that ^{80}Br reacts principally *via* the energetic processes in these binary systems; this supports the assumptions that the relative IP of the atmosphere is a major controlling factor in determining the relative important of the thermal ionic processes of ^{80}Br.

An attempt has also been made to compare the reactivity of two kinds of C–H bonds in C_3H_8, since corrections for the ^{80}Br spectrum are not required except for the secondary decomposition of the primary products.

Experimental

The general experimental procedure is the standard one for recoil Br atom reactions,[4] involving the formation of ^{80}Br from the ^{80}Br(I. T.)^{80}Br nuclear reaction and the subsequent analysis of the radioactive products by radio gas chromatography. The total pressure was usually 700 ± 10 Torr except in the pressure-effect experiments. The ratio of Br_2 relative to the reactant was 0.02 ± 0.01 throughout the work.

Materials. The ethane and propane were supplied by the Takachiho Chemical Co. with nominal purities of 99.9% and 99.7%; they were used after washing with concentrated sulfuric acid and after purification by vacuum distillation. Methyl bromide from the Tokyo Kasei Co. was purified several times by vacuum distillation.

Addition of O_2. Initially many runs were made without the addition of O_2 to the reaction systems. The values of the yields of the products from the reaction of ^{80}Br with C_3H_8, particularly that for the yield of i-$C_3H_7{}^{80}Br$, were not reproducible. This was probably due to the reaction of the C_3H_6 present in C_3H_8 as an impurity with the irradiated Br_2. However, reproducible results were obtained when 65 Torr of O_2 was added to the reaction mixture at the beginning of the reactions.

Percent Yields. The propane used in the present work contains very little C_3H_6, but even this amount of propylene interferes with the measurement of the total organic yield from the systems containing C_3H_8 as a reactant. Thus the absolute yield has been measured only from the ^{80}Br-C_2H_6-$O_2(3.2\pm0.1\%)$ and ^{80}Br-CH_3Br-$O_2(2.5\pm0.1\%)$ systems 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 correction factor determined from the sum of the relative yields and from the total organic yield found in the above systems. The radio gas chromatograms were analyzed on a FACOM 230—60 computor in order to obtain the relative yields of the products, using the BOB 7 series program[7] corrected for the background and for the radio-activity decay of nuclides.

1) R. Wolfgang, Progr. *Reaction Kinetics*, **3**, 97 (1965).
2) J. B. Nicholas and E. P. Rack, *J. Chem. Phys.*, **48**, 4085(1968).
3) J. Okamoto and E. Tachikawa, This Bulletin, **42**, 1504 (1969).
4) E. Tachikawa and T. Kahara, *ibid.*, **43**, 1293 (1970).
5) M. Yagi, K. Kondo, and T. Kobayashi, *ibid.*, **44**, 580 (1971).
6) E. Tachikawa and K. Yanai, *Radiochim. Acta*, **17**, 138 (1971).
7) H. Baba, H. Okashita, S. Baba, T. Suzuki, and H. Umezawa, *J. Nucl. Sci. Technol.*, **8**, 703 (1971).

Table 1. ^{80}Br stabilized in organic combination in Kr-moderated system

C_3H_8 (mmHg)	$\frac{C_3H_8}{C_3H_8+Kr}$	$CH_3{}^{80}Br$ (%)	$C_2H_5{}^{80}Br$ (%)	i-$C_3H_7{}^{80}Br$ (%)	n-$C_3H_7{}^{80}Br$ (%)	$CH_2{}^{80}BrBr$ (%)
594	0.945	1.0	0.53	0.21	0.64	0.40
551	0.869	1.0	0.54	0.26	0.60	0.36
448	0.695	0.84	0.45	0.22	0.46	0.37
399	0.592	0.86	0.36	0.15	0.39	0.31
349	0.529	0.74	0.35	0.08	0.25	0.21
307	0.467	0.85	0.29	0.11	0.28	0.20
300	0.449	0.75	0.31	0.12	0.28	0.19
200	0.310	0.59	0.15	0.10	0.13	0.16
118	0.167	0.66	0.11	0.05	0.09	0.12
100	0.150	0.63	0.11	0.09	0.07	0.05

Table 2. Percent ^{80}Br stabilized in organic combination in various binary mixtures

Press of C_3H_8	$\frac{C_3H_8}{C_3H_8+\text{additive}}$	$CH_3{}^{80}Br$ (%)	$C_2H_5{}^{80}Br$ (%)	i-$C_3H_7{}^{80}Br$ (%)	n-$C_3H_7{}^{80}Br$ (%)	$CH_2{}^{80}BrBr$ (%)
Additive: C_2H_6						
630	1.000	1.2	0.57	0.20	0.67	0.47
558	0.877	1.2	0.65	0.19	0.60	0.44
508	0.795	1.3	0.60	0.17	0.56	0.41
446	0.697	1.1	0.75	0.13	0.45	0.43
410	0.642	1.3	0.84	0.21	0.50	0.50
311	0.494	1.4	0.93	0.15	0.44	0.45
266	0.417	1.4	0.82	0.15	0.37	0.34
200	0.317	1.3	0.95	0.13	0.33	0.46
169	0.264	1.3	0.94	0.07	0.17	0.37
127	0.199	1.4	1.0	0.07	0.18	—
98	0.155	1.5	1.2	0.06	0.15	0.53
61	0.105	1.4	1.2	0.06	0.09	0.43
27	0.042	1.5	1.3	0.02	0.04	0.42
—	0.000	1.5	1.2	—	—	0.39
Additive: CH_3Br						
590	0.941	1.1	0.50	0.20	0.58	0.41
510	0.819	1.1	0.38	0.17	0.45	0.40
454	0.723	1.1	0.39	0.14	0.38	0.36
428	0.596	1.1	0.30	0.14	0.36	0.52
362	0.572	1.3	0.30	0.13	0.35	0.62
317	0.508	1.4	0.26	0.18	0.27	0.58
272	0.437	1.3	0.19	0.08	0.22	0.53
220	0.348	1.4	0.19	0.10	0.19	0.73
180	0.287	1.6	0.08	0.06	0.12	0.64
126	0.203	1.5	0.10	0.04	0.10	0.67
66	0.105	1.5	0.07	0.02	0.05	0.80
—	0.000	1.6	—	—	—	0.87

Results and Discussion

The five chief organic products observed from the reactions of (I. T.)-activated ^{80}Br with C_3H_8 were $CH_3{}^{80}Br$, n-$C_3H_7{}^{80}Br$, $C_2H_5{}^{80}Br$, i-$C_3H_7{}^{80}Br$, and $CH_2{}^{80}BrBr$. Table 1 summarizes the yields of the individual products obtained from the Kr-moderated systems. The yields of $C_2H_5{}^{80}Br$, n-$C_3H_7{}^{80}Br$, and $CH_2{}^{80}BrBr$ decreased with the increase in the m. f. of Kr, and could be extrapolated to zero at 1.0 m. f. of Kr. However, the $CH_3{}^{80}Br$ and i-$C_3H_7{}^{80}Br$ yields were extrapolated to 0.6±0.1% and 0.05±0.02% respectively. If one simply assigns these limiting yields at 1.0 m. f. of Kr as the thermal ionic yields, both $CH_3{}^{80}Br$ and i-$C_3H_7{}^{80}Br$ are found to be formed by two processes. One involves an excess kinetic energy, and the other, thermal ionic processes. The other products are principally formed *via* energetic processes of ^{80}Br. This simple assignment does not necessarily indicate the true reaction processes involved in the reactions of ^{80}Br in the C_3H_8 atmosphere, as has been discussed in our previous paper.[6] Since the IP of Kr is considerably higher than that of Br, the presence of the large amount

of Kr in the reaction system influences the charge neutralization as well as the energy degradation of ^{80}Br; thus, the charge and the kinetic energy distribution of ^{80}Br in the reaction energy range is different from those of a system with no additives. Thus, the results shown in Table 1 can firm that fractions of $CH_3{}^{80}Br$ and i-$C_3H_7{}^{80}Br$ are formed *via* thermal ionic processes in a highly Kr-moderated system.

As an alternative approach to the true reaction processes involved in the C_3H_8 atmosphere, one can study a binary system, using C_2H_6 or CH_3Br as a counterpart. The IP's of the constituents are 11.21 eV for C_3H_8, 11.65 eV for C_2H_6, and 10.6 eV for CH_3Br, compared to 11.84 eV for Br.[8] If the identity of the reacting ^{80}Br is primarily controlled by the IP of the constituents of the reaction systems, it is seems that the thermal ionic processes are of only minor importance in these binary systems. Thus, the yields of the products from one of the constituents will decrease with an increase in the m. f. of the other and can be extrapolated to zero at 1.0 m. f. of the latter. However, if this is not the case, the yields, as a function of the diluent, will reflect the thermal ionic processes.

Table 2 summarizes the yield-variation of products from various mixtures of C_3H_8 and C_2H_6, and from those of C_3H_8 and CH_3Br. *Iso-* and n-$C_3H_7{}^{80}Br$ were formed only from the reaction of ^{80}Br with C_3H_8, and their yields decreased smoothly from 0.20 ± 0.02 and 0.67 ± 0.07 respectively with the addition of the diluent to zero percent. However, in the C_3H_8–C_2H_6 mixtures, $CH_3{}^{80}Br$, $C_2H_5{}^{80}Br$, and $CH_2{}^{80}BrBr$ were formed from the reactions with either constituent and the sum of the yields was the same as the observed yields of these products. Similarly, in the C_3H_8–CH_3Br mixture, $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ were products from both constituents.

A separation of the observed yield at any m. f. of C_3H_8 into the yields originating from the individual constituents can be performed on two assumptions; one, that the thermal ionic yield is zero over the whole range of m. f. of C_3H_8, and the other, that the relative yield distribution among the products from the reactions with C_3H_8 is constant over the range of m. f. of C_3H_8. The first assumption is rather probable in view of the IP's of the constitutents involved. The second assumption, however, is a crude one, since the ratio of n-$C_3H_7{}^{80}Br/i$-$C_3H_7{}^{80}Br$ tends to vary slightly with the m. f. of the diluents(see below). However, the variation is only significant at a small m. f. of C_3H_8, where the yields of products from C_3H_8 are small. This amount of variation in the yield distribution, thus, will have only a minor influence on the subsequent discussion.

With these assumptions, the yields of these products at any m. f. of C_3H_8 can be calculated by multiplying the percentage yield of n-$C_3H_7{}^{80}Br$ by 1.8 for $CH_3{}^{80}Br$, by 0.85 for $C_2H_5{}^{80}Br$, and by 0.70 for $CH_2{}^{80}BrBr$. The solid curves in Figs. 1 and 2 indicate the calculated yields of these products from the reactions with C_3H_8.

8) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York (1957), Appendix.

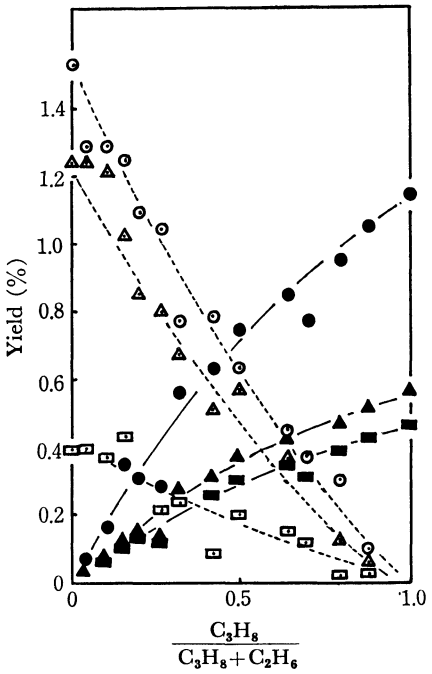

Fig. 1. Estimated yields from the reactions of ^{80}Br with C_3H_8 and C_2H_6 in the binary systems.
●: $CH_3{}^{80}Br$ from C_3H_8, ▲: $C_2H_5{}^{80}Br$ from C_3H_8,
■: $CH_2{}^{80}BrBr$ from C_3H_8, ⊙: $CH_3{}^{80}Br$ from C_2H_6,
△: $C_2H_5{}^{80}Br$ from C_2H_6, ⊡: $CH_2{}^{80}BrBr$ from C_2H_6.

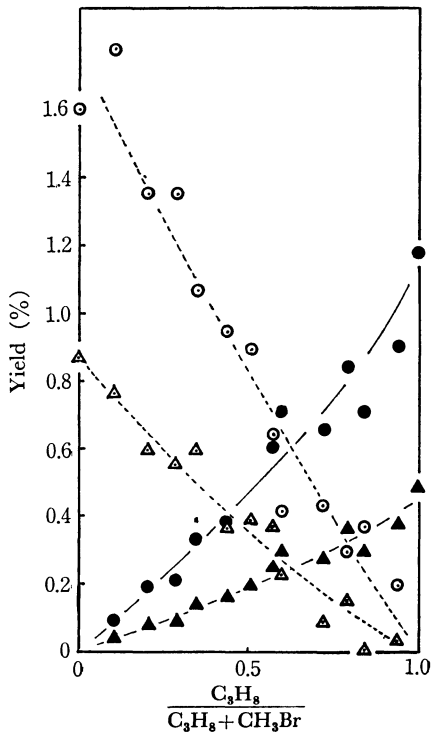

Fig. 2. Estimated yields from the reaction of ^{80}Br with C_3H_8 and CH_3Br in the binary systems.
●: $CH_3{}^{80}Br$ from C_3H_8, ▲: $CH_2{}^{80}BrBr$ from C_3H_8,
⊙: $CH_3{}^{80}Br$ from CH_3Br, △: $CH_2{}^{80}BrBr$ from CH_3Br

The dotted curves in the same figures are simply obtained from the difference between the calculated yields and the experimentally-determined yields at each measureing point and are assigned to the yield curves from the reactions with C_2H_6 or CH_3Br.

These results show that the yields of products which originated from either C_2H_6 or CH_3Br decreased zero upon the addition of C_3H_8, and that it is rather difficult to detect any interference of possible thermal ionic process in the yield variation. This implies that the thermal ionic process is not important in the present binary systems (see Appendix).

The oxygen added to suppress the radical formations of organic compounds amounts to roughly 9% of the reaction mixture. The IP of O_2 is intermediate between the first and the second IP of Br. Thus, its presence possibly influences the ^{80}Br spectrum towards preferring the formation of the thermal $^{80}Br^+$ ion. However, the influence will be smaller than that to be expected simply from its mole fraction judging from the point of the collision cross section for the ^{80}Br-O_2 and ^{80}Br-reactant molecule collisions. The analysis of the results (see Figs. 2 and 3) shows no positive evidence for the contribution of the thermal ionic process. Thus, it is conclusive that ^{80}Br reacts principally *via* the energetic processes to form organic compounds in the C_3H_8, C_2H_6, and CH_3Br atmospheres. However, when these reactants are diluted with a sufficiently large excess of Kr having a IP of 14.00 eV, the energy degradation and the charge neutralization of ^{80}Br are controlled through its collision with Kr. The thermal $^{80}Br^+$ was eventually obtained,[9] and its reaction became important. Those conclusions are consistent with the previous speculation[6] that the thermal ionic processes of ^{80}Br are almost negligible in a reaction system with a lower IP than that of Br.

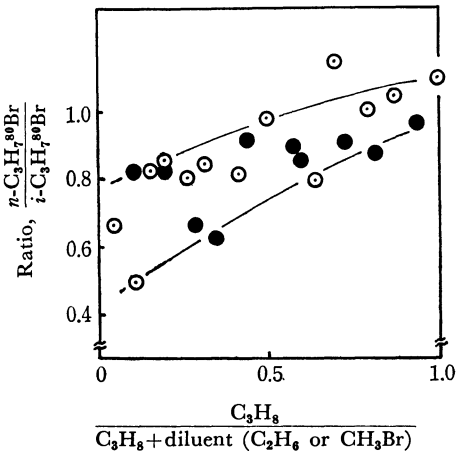

Fig. 3. Variation of n-$C_3H_7{}^{80}Br/i$-$C_3H_7{}^{80}Br$ per bond basis as a function of concentration of C_3H_8, relative to diluent.
⊙: C_3H_8-C_2H_6-O_2 system, ●: C_3H_8-CH_3Br-O_2 system

Reactivity of Primary and Secondary C–H Bonds in C_3H_8. In the recoil atom reactions, the chemical factors often play an important role in controlling the reactivity of various bonds. Two main difficulties have usually confronted such experiments: 1) the attainment of the "equivalent experimental conditions" for the comparison of the various chemical bonds, and 2) the failure of all of the molecules formed in the primary reactions to survive long enough to be measured.[10] The most important problem in trying to equalize conditions for an inter- or intra-comparison of different samples is in controlling the number and distribution *vs.* the energy of the hot collisions potentially available to an energetic atom prior to thermalization.[11–13] The cumulative absolute yield from a particular hot atom reaction is a function not only of the other hot reactions available to the energetic atom at all energies, but also of the rate of energy loss for the atom in nonreactive collisions. The measurement of the relative yields in an intramolecular system, however, ensures that each hot atom sums over the identical recoil atom spectrum and is free from the problem.

Propane includes both primary and secondary C–H bonds in a molecule, thus permitting a direct comparison of the reactivities of these C–H bonds toward the energetic ^{80}Br atom. The ^{80}Br *for H* reaction gives n- and i-$C_3H_7{}^{80}Br$, depending upon which kind of C–H bond is attacked. The bond dissociation energies are 4.23±0.04 eV for primary, and 4.1± 0.02 eV for secondary, C–H bonds.[14] If the chemical characteristics, including the bond strength, have some correlation with the reactivity toward the energetic ^{80}Br, it may appear in the relative yields of n- and i-$C_3H_7{}^{80}Br$.

Figure 3 shows the variation in the n-$C_3H_7{}^{80}Br/i$-$C_3H^{80}Br$ per bond basis as function of $C_3H_8/(C_3H_8+$ diluent) in the mixed system with C_2H_6 or CH_3Br. One can discuss the results without any correction for the ^{80}Br-spectrum, but they must be corrected for the decomposition reactions of the primary products. The most probable decomposition pathway both for n- and i-$C_3H_7{}^{80}Br$ is the elimination of $H^{80}Br$ to form

Table 3. Effects of the total pressure on the yields of n-$C_3H_7{}^{80}Br$ and i-$C_3H_7{}^{80}Br$ (Br_2/C_3H_8= 0.02 and O_2/C_3H_8=0.1)

Total pressure	i-$C_3H_7{}^{80}Br$ (%)	n-$C_3H_7{}^{80}Br$ (%)	$\frac{n\text{-}C_3H_7{}^{80}Br}{i\text{-}C_3H_7{}^{80}Br}$ (per bond basis)
55	0.12	0.17	0.47
211	0.17	0.43	0.84
337	0.17	0.43	0.84
558	0.19	0.55	0.96
698	0.21	0.66	1.1
710	0.20	0.67	1.1
773	0.20	0.69	1.2
1052	0.27	0.76	0.94
1600	0.27	0.83	1.0

9) F. Cacace and G. Stocklin, *J. Amer. Chem. Soc.*, **94**, 2518 (1972).

10) Y. N. Tang and F. S. Rowland, *ibid.*, **87**, 3304 (1965), **90**, 574 (1968).

11) Y. N. Tang, E. K. C. Lee, E. Tachikawa, and F. S. Rowland, *J. Phys. Chem.*, **75**, 1290 (1971).

12) E. K. C. Lee and F. S. Rowland, *J. Amer. Chem. Soc.*, **85**, 2907 (1963).

13) C. C. Chou and F. S. Rowland, *J. Phys. Chem.*, **75**, 1283 (1971).

14) E. Tachikawa, Ph, D. Thesis, Univ. of Calif., Irvine, (1967), p. 181.

C_3H_6. Such unimolecular reactions can be conveniently investigated through pressure variation experiments; the present pressure-dependent data are shown in Table 3. The yields of both *n*- and *i*-$C_3H_7{}^{80}Br$ increased with an increase in the pressure. The ratio between them also increased, with a preference toward *n*-$C_3H_7{}^{80}Br$, at the beginning, but tended to be constant at 1.1 ± 0.1 over a total pressure of 600 Torr. However, this value does not necessarily indicate the real yield ratio of the primary reactions, since the correct estimation must be based on measurements of their secondary decomposition products, measurements are not possible in this type of experiment. In the present semiquantitative consideration, no correction has been made for the secondary decompositions of the primary products, since no a priori basis for estimating a correction factor exists. Recent theoretical knowledge indicates that more than one chemical bond is involved in the substitution reaction of an energetic atom.[15] Furthermore, the intramolecular distribution of the excitation energy is attained within a few vibrations. Thus, even if the secondary decomposition of the primary products still occur at pressures higher than 600 Torr, the yield ratio of *n*-$C_3H_7{}^{80}Br$/*i*-$C_3H_7{}^{80}Br$ should be much less sensitive to the applied pressure.

With these allowances, one can notice a positive dependence of the ratio on the concentration of C_3H_8, although the points deviate considerably. The ratio is 1.1 ± 0.1 with no dilution, and seems to decrease with the diluent. This qualitatively implies that the difference in reactivities of two kinds of C–H bonds for ^{80}Br is not significant in the distribution spectrum of the ^{80}Br controlled by collisions, principally with C_3H_8, but that the reactivity of secondary C–H bonds relative to primary C–H bonds increases with the dilution. While the effects on energy moderation by an inert gas are relatively simple to evaluate, the effects of dilution by a second reagent are much more complex, since such a reagent influences the ^{80}Br-spectrum through both kinetic-energy moderation and reactive collisions. The total organic yields from systems variously diluted with a second reagent, however, are always very small, as may be seen in Table 2; this, the elimination of ^{80}Br through reactions with the diluent cannot be important in the present qualitative discussion. As dilution with the diluent proceeds, the kinetic energy spectrum of ^{80}Br available for the reactions with C_3H_8 tends to shift to the lower-energy end and the lower-energy process becomes preferred over the high-energy process. Thus, one can tentatively conclude that the formation of *i*-$C_3H_7{}^{80}Br$ is a lower energy process than the formation of *n*-$C_3H_7{}^{80}Br$.

The efficiency of the kinetic energy moderation varies depending upon the additive used in the binary systems. Thus, the rate of decrease in the *n*-$C_3H_7{}^{80}Br$/*i*-$C_3H_7{}^{80}Br$ ratio with dilution should be correlated with the additives used. Unfortunately, the scattering of the results exceeds the possible variation in the ratio due to the different moderating efficiency of the diluent.

The relative position of the energy range of the reactions with two kinds of C–H bonds is consistent with the pressure dependence of the yields of the reaction products. The failure of the billiard-ball type of approximation in the recoil atom reaction implies that the internal excitation energy of the primary substitution reaction products is a good guide for the average kinetic energy of the recoil atom at the time of reaction.[16–18] As the total pressure rises, the stabilization of the excited products become more probable. Thus, an increase in the *n*-$C_3H_7{}^{80}Br$/*i*-$C_3H_7{}^{80}Br$ ratio with the pressure will be reflected in the fact that *i*-$C_3H_7{}^{80}Br$ is less excited and has a longer life-time, than *n*-$C_3H_7{}^{80}Br$.

The present results thus furnish evidence that the secondary C–H bond is more subject to the *^{80}Br for H* reaction than is the primary C–H bond under kinetic-energy-moderated conditions. Although this is consistent with the C–H bond strength effect involving the higher reactivity of the weaker C–H bond than that of the stronger C–H bond, no definite impormation has been obtained here concerning the identity of the chemical nature affecting the reactivities of two kinds of C–H bonds.

The trend toward higher yields for reactions with less sterically obstructed C–H would favor a higher yield for *n*-$C_3H_7{}^{80}Br$ than that for *i*-$C_3H_7{}^{80}Br$, this is not supported by the experimental observations. If such a steric factor is also opperative in the present experiment, the assessment of the importance of the chemical nature must be increased by an equivalent counterbalancing factor.

Appendix

The kinetic theory for energetic atom reactions was developed by Wolfgang *et al.*[10,20] and has since been applied to various systems.[21] The assumptions involved in its application to the reaction systems of ^{80}Br have been discussed by Milman.[22] Success depends on the assumptions that neither S nor α is a function of the recoil atom energy, or that, if they are, the energy variations are slight and the function smooth. Another important assumption is that the initial energy of the recoil atom is sufficiently high for the atoms to have made a number of collisions in order to attain the statistical distribution of energies for the atoms in the reaction range. The average kinetic energy of the Br atom achieved from the molecular explosion of Br_2 can be estimated to be up to 100 eV, based upon the Coulombic interaction energy. Since our knowledge about the kinetic energy spectrum of Br is not yet complete, we assume this

15) D. L. Bunker and M. Pattengill, *Chem. Phys. Lett.*, **4**, 315 (1969), *J. Chem. Phys.*, **53**, 3041 (1970).

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19) P. J. Estrup and R. Wolfgang, *J. Amer. Chem. Soc.*, **82**, 2665 (1960).

20) R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

21) E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).

22) M. Milman, *Radiochim. Acta*, **2**, 180 (1964).

to be reasonably justified in our case.

The developed equation for the yields of individual products from energetic reactions with a reactant in the moderated system, P_i, is:

$$P_i = \frac{f_i}{\alpha} I_i - \frac{f_i^2}{\alpha^2} K_i + \frac{f_i^3}{\alpha^3} L_i - \quad (1)$$

where f and α have their usual meanings.

Unless the total reactivity of the system is very high, the series will converge rapidly. In systems of a very low reactivity, as in the present case, only the first may be sufficient.

Table 4. Relative α-values in the ^{80m}Br-C_3H_8-C_2H_6 and ^{80m}Br-C_3H_8-CH_3Br systems

In C_3H_8-C_2H_6 system compound	intercept $\alpha(R)/I_i$	slope $\alpha(M)/I_i$	$\frac{\alpha(C_3H_8)}{\alpha(C_2H_6)}$
i-$C_3H_7{}^{80}Br$ from C_3H_8	4.0	4.0	1.0
n-$C_3H_7{}^{80}Br$ from C_3H_8	1.4	1.3	1.1
$CH_3{}^{80}Br$ from C_2H_6	0.66	0.68	1.0
$C_2H_5{}^{80}Br$ from C_2H_6	0.78	0.84	1.1
$CH_2{}^{80}BrBr$ from C_2H_6	2.4	3.7	1.5
			av. 1.1±0.2
In C_3H_8-CH_3Br system compound	intercept $\alpha(R)/I_i$	slope $\alpha(M)/I_i$	$\frac{\alpha(C_3H_8)}{\alpha(CH_3Br)}$
i-$C_3H_7{}^{80}Br$ from C_3H_8	4.8	6.3	0.76
n-$C_3H_7{}^{80}Br$ from C_3H_8	1.8	2.6	0.69
$C_2H_5{}^{80}Br$ from C_3H_8	2.1	2.6	0.81
$CH_3{}^{80}Br$ from CH_3Br	0.56	0.47	0.83
$CH_2{}^{80}BrBr$ from CH_3Br	1.2	0.88	0.74
			av. 0.77±0.06

Table 5. ^{80}Br recoil energies resulting from coulombic repulsion of $^{80m}BrBr$

Original charge on bromine	^{80}Br recoil energies (eV)
+2	3.2
+4	9.6, 12.9
+6	16.1, 25.8, 29.0
+8	22.4, 38.5, 48.2, 51.4
+10	29.0, 51.4, 68.0, 77.0, 80.4
+12	35.3, 64.3, 86.7, 102.7, 115.6

Thus, in a moderated system Eq. (1) may be modified to this equation:

$$\frac{1}{P_i} = \frac{\alpha(R)}{I_i} + \frac{\alpha(M)}{I_i}\left[\frac{f(M)+Af(O_2)}{f(R)}\right] \quad (2)$$

where $A=\alpha(O_2)/\alpha(M)$; when M is C_2H_6, $A=0.72$ was obtained using the results in Ref. 6). When we plot $1/P$ *vs.* $[f(M)+Af(O_2)]/f(R)$, the slope is $\alpha(M)/I_i$ and the intercept is $\alpha(R)/I_i$. The ratio of these gives $\alpha(M)/\alpha(R)$.

The results shown in Figs. 1 and 2 have been used for the kinetic treatment according to Eq. (2). Table 4 summarizes the $\alpha(M)/I_i$, $\alpha(R)/I_i$, and $\alpha(M)/\alpha(R)$ thus obtained. In the present kinetic analysis two important requirements are not fully satisfied. One of these is that, because the initial kinetic energy is relatively low (see Table 5) the equilibrium distribution of ^{80}Br can not be attained in the reaction energy range. The other is the exclusion of the energetic-$H^{80}Br$ yield from the considerations, which will introduce a serious error if we ignore the higher terms in Eq. (1). Despite these difficulties, reasonably consistent values are obtained for both $\alpha(M)/\alpha(R)$ values. These, in turn, indicate that the above assumptions are reasonably satisfied and that the present kinetic analysis is justified within our limits of experimental accuracy.