Table II. Parameters Used in Extended Hückel Calculations

orbital		H_{ii}, eV	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
V	3d	−11.00	4.70	1.70	0.4755	0.7052
	4s	−8.81	1.30			
	4p	−5.52	0.875			
Mo	4d	−11.06	4.54	1.90	0.5899	0.5899
	5s	−8.77	1.96			
	5p	−5.60	1.90			
W	5d	−10.37	4.982	2.068	0.6685	0.5424
	6s	−8.26	2.341			
	6p	−5.17	2.309			
P	3d	−7.00	1.40			
	3s	−18.60	1.60			
	3p	−14.00	1.60			
S	3s	−20.00	1.817			
	3p	−13.30	1.817			
Cl	3s	−30.00	2.033			
	3p	−15.00	2.033			

[a] Coefficients in a double-ζ expansion.

In general, a given ML_2 subunit, e.g., $M(CO)_2$, generates a double minimum in the total energy. In one configuration the ligands move together and in the other they move apart. The singling out of one of these two minima as the deeper one for a specific molecule is a consequence of the composite effect of the ML_2, ML_2', and ML_2'' subunits.

We found we could rationalize the observed C_{2v} deformations. The understanding that we achieved and the procedure evolved in this analysis is, however, more important than the specific molecules which led us to the problem. The way is clear to an analysis of deformations in any coordination geometry, for any d-electron configuration.

Acknowledgment. We are grateful to J. L. Templeton for bringing several structures to our attention and to him and M. H. Chisholm for informing us of their work prior to publication. Helpful comments were made by the referees. Thanks are due to IREX for making possible the stay of Pavel Kubáček at Cornell, the National Science Foundation for its generous support of our work through research Grant CHE 7828048, and the Materials Science Center at Cornell University, (MSC Grant DMR-7681083). Pavell Kubáček would like to express his appreciation for the hospitality of our research group at Cornell. We are grateful to J. Jorgenson for the drawings and O. Eisenstein and D. Hoffman for their help in the processing of this paper.

Appendix

All calculations were performed by using the extended Hückel method,[29] with weighted H_{ij}'s.[30] Unless mentioned the experimental bond lengths were used.

The values for the H_{ii}'s and orbital exponents are listed in Table II. The parameters for C, N, O, and H are the standard ones.[29]

---

[29] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179–2195; **1962**, *37*, 2872–2883.

[30] Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686–3692.

Reactions of Recoil Bromine Formed by the $^{76,77}Kr \rightarrow {}^{76,77}Br$ Systems with Simple Hydrocarbons. Solid-Phase Reactions[1]

James J. Frost, Stephen M. Moerlein, and Michael J. Welch*[2]

Contribution from the Mallinckrodt Institute of Radiology, Washington University School of Medicine, St. Louis, Missouri 63110. *Received July 31, 1980*

Abstract: Bromine atoms formed by the systems $^{76}Kr \rightarrow {}^{76}Br$ and $^{77}Kr \rightarrow {}^{77}Br$ were allowed to react with simple hydrocarbons in the solid phase at 77 K and the products of the reactions studied. The product distributions for the two systems varied greatly, and these variations are discussed in terms of the charge and kinetic energy of the two recoiling bromine species. It is concluded that the product differences are due to altered radical environments arising from charge neutralization for ^{76}Br and recoil energy dissipation for ^{77}Br.

In this study activation of bromine atoms from krypton decay will be considered. The parent–daughter systems used to generate such bromine atoms are

$$^{76}Kr \xrightarrow{EC} {}^{76}Br$$

$$^{77}Kr \xrightarrow{\beta^+/EC} {}^{77}Br$$

Relevant physical data for these processes are shown in Table I.

These two systems are interesting to compare because the decay mode and energy released in each process is different, leading to contrasts in the initial charge states and recoil energies of the two bromine atoms. As shown in Table I, the recoil energies are 7.5 eV for ^{76}Br, 67.5 eV for electron-capture decay formation of ^{77}Br, and 7.2 eV (average; 37.8-eV maximum) for positron decay formation of ^{77}Br.

Determination of the initial charge states is somewhat more complicated. For the electron-capture case, the atom is formed with a high positive charge (average ~5+) due to inner-shell electron-capture process and the subsequent electron cascade which results in the emission of Auger electrons and x radiation.[8] For the case of positron decay the atom would simply be left with a net 1− charge due to the loss of the 1+ charged positron. Therefore all of the ^{76}Br atoms would be formed with at least a 1+ charge since ^{76}Kr decays nearly 100% via electron capture. For the ^{77}Br case, 16% would be formed as in the ^{76}Br case and 84% would initially be formed as $^{77}Br^-$. There are two factors which modify these considerations to give the net charge spectra shown in Figure 1 for ^{77}Br and Figure 2 for ^{76}Br. These are the processes of electron shake-off and internal conversion of the γ-rays from the excited bromine nuclei.

---

[1] This work was supported in part by NIH Grants HL13851 and HL14147.

[2] To whom correspondence should be addressed.

[3] Lederer, C. M.; Shirley, V. S. "Table of Isotopes", 7th ed.; Wiley; New York, 1978.

[4] Lode, D.; Pessara, W.; Ohlsson, H.; Roeckl, E. *Z. Phys.* **1973**, *260*, 253.

[5] Sarantites, D. G.; Braga, R. A. *Phys. Rev. C* **1974**, *9*(4), 1493.

[6] Roeckl, E.; Lode, D.; Bachmann, K.; Neidhart, B.; Wolk, G. K.; Lauppe, W.; Kafrell, N.; Patzelt, P. *Z. Phys.* **1974**, *226*, 65.

[7] Stocklin, G. "Chemie Heisser Atome"; Verlag Chemie: Weinheim, West Germany, 1969.

[8] Carlson, G. A. "Photoelectron and Auger Spectroscopy"; Plenum Press: New York, 1975.

0002-7863/81/1503-4332$01.25/0 © 1981 American Chemical Society

Table I. Decay Characteristics of Kr → Br Systems

	^{76}Kr	^{76}Br	^{77}Kr	^{77}Br
decay mode	EC	β^+/EC	β^+/EC	β^+/EC
β^+/EC[a]		1.326	5.25	0.007
major γ-rays (intensities)	0.04550 (273) 0.2522 (100) 0.2704 (307) 0.3158 (583) 0.4065 (175) 0.4521 (135)[b]	0.55991 (100) 0.65700 (21.4) 1.21610 (12.00) 1.85368 (19.3) 2.95055 (10.50)[a]	0.1297 (100) 0.1465 (46.4) 0.2762 (3.81) 0.3122 (4.27)[c]	0.23898 (100) 0.29723 (18.0) 0.52069 (97.0) 0.57891 (12.8)[a]
half-life	14.82 h[b]	16.1 h[a]	74.7 min[c]	57.04 h[a]
E_{β^+}(max), MeV			1.875[a]	
Q_{EC}, MeV	1.2[b]		3.3[d]	
recoil energy of daughter,[e] eV	7.5 eV		β^+ 37.8 eV (max), 7.2 eV (av), EC 67.5 eV	
$I_{\gamma\pm}/I_{\gamma}$[a]		1.45 (for 0.559-MeV line)		0.635 (for 0.239-MeV line)

[a] Reference 3. [b] Reference 4. [c] Reference 5. [d] Reference 6. [e] Calculated from expressions in ref 7.

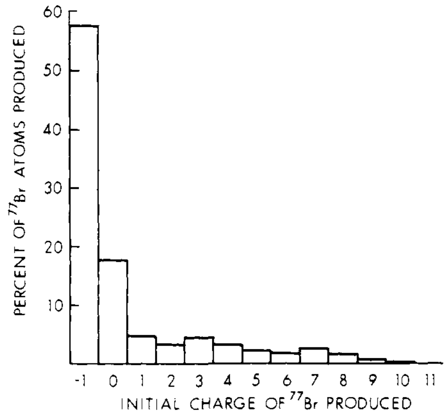


Figure 1. Charge spectrum for bromine-77 produced by the process $^{77}\mathrm{Kr}\xrightarrow{\beta^+/\mathrm{EC}}{}^{77}\mathrm{Br}$.

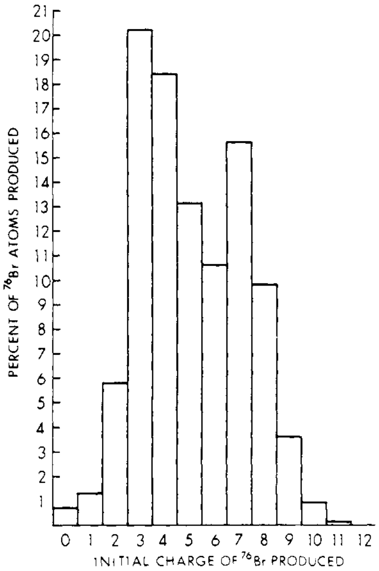


Figure 2. Charge spectrum for bromine-76 produced by the process $^{76}\mathrm{Kr}\xrightarrow{\mathrm{EC}}{}^{76}\mathrm{Br}$.

Electron shake-off involves the loss of predominantly outer-shell electrons due to a sudden change in the atomic charge.[8] This process occurs to some extent in both the EC and positron decays but is more important from our standpoint in the positron decays. In the EC decays most of the charging occurs due to the Auger process, and electron shake-off modifies the charge spectrum to only slightly higher charges. This is not very important since the charge must be reduced to at most 1+ before reaction can take place. However, in the positron case the shake-off process creates both some neutral and some positively charged bromine which would be expected to display reactivities different from each other and from Br$^-$.

The other factor which brings about a change in the charge spectrum is internal conversion. Both EC or β^+ decay form excited bromine nuclei which can deexcite by emission of a γ-ray or by internal conversion, in which case an inner-shell electron is emitted instead of the photon. Thus an inner-shell vacancy is created and a vacancy cascade with high charging takes place. Again, this process is more important for the positron decay process in its effects on the charge spectrum. In addition, ^{77}Br has a metastable state with a half-life of approximately 4.2 min.[3] This state deexcites via an E3 transition either by the emission of a 105.6-keV γ-ray or 87.6% of the time by internal conversion.[9] Approximately 10% of all ^{77}Kr decays through this state. In addition, about 4.1% of ^{77}Kr decays via a 24.2-keV E2 transition of ^{77}Br which will be approximately 98% converted.[3]

This method of first producing the carrier-free parent isotopes and then studying the results of the decay process has some important advantages over systems previously used. First, the reaction mixtures are not exposed to any reactor or cyclotron radiation since the decaying krypton isotopes are mixed with the substrate after the irradiation is finished. Second, no carrier amounts of any additional compounds such as ^{80m}BrBr need be added to the reaction mixture and therefore mechanistic evaluations are simpler. Third, the conditions of the reaction mixture can be varied more easily since direct irradiations do not take place. Thus reactions at very high pressure can be studied by using this method. Also, reactions in solid low molecular weight hydrocarbons or other volatile hydrocarbons can be studied at 77 K by freezing them together with the krypton isotopes. Both of these types of experiments would be quite difficult in a reactor or by using a cyclotron.

Experimental Section

The krypton isotopes were produced via the (^{3}He,3n) reaction by the bombardment of selenium with ^{3}He. Natural selenium was used since the natural isotope abundances of ^{76}Se and ^{77}Se (9.02% and 7.58%, respectively) are high enough to give large quantities of ^{76}Kr and ^{77}Kr. Some ^{77}Kr was also produced by the ^{76}Se(^{3}He,2n)^{77}Kr reaction.

A cooled target was used so that the krypton did not evaporate from the selenium target during the irradiation. Liquid nitrogen in a Dewar container above the target was in direct contact with a copper block, into which was screwed a copper target containing selenium. The selenium powder was held in place by a piece of 0.025 mm thick Dural aluminum foil. All materials between the liquid nitrogen and the selenium were constructed of copper to provide rapid transfer of heat. After the irradiation at the Washington University 52 in. cyclotron (normal conditions: 1-2 h, 3-5 μA, 25-MeV ^{3}He), the target was removed and the krypton was evolved by heating the selenium. Sample preparation was as follows. The selenium was removed from the copper target after the irradiation and placed in a glass vessel which was connected to a vacuum line and evacuated. Even though a cooled target was used, the selenium, which was initially a powder, was melted to some extent (mp 217 °C) by the ^{3}He beam. After the bombardment is concluded, the selenium quickly

---

(9) Houdayer, A.; Mark, S. K.; Kitching, J. E.; Paradellis, T. *Phys. Fenn.* **1974**, *9*, 85.

resolidifies, thus trapping the krypton within a solid matrix of selenium. For this reason, little krypton was lost either during the evacuation procedure or during the transportation of the selenium from the cyclotron to the laboratory, even though the selenium is then at room temperature.

After the vessel containing the selenium was completely evacuated, the selenium was heated to its boiling point and the krypton evolved. The krypton gas was Toepler-pumped through a trap at −130 °C (a pentane slush) to remove any ^{76}Br and ^{77}Br produced by previous krypton decays, as well as any other volatile matter liberated during the heating which might interfere with the reactions under study.

After the reaction vessels were filled with krypton, the other components were added by using standard vacuum line techniques. Long (approximately 20 cm), narrow (approximately 3-4-mm i.d.) glass vessels fitted with a Teflon valve were used. In these experiments a quantity of hydrocarbon and krypton was frozen into a bolus at the bottom of the tube by using liquid nitrogen. Even though the level of the liquid nitrogen falls during the time that the sample was kept frozen, the bottom of the tube always remained submerged. In this way the samples could be kept frozen almost 1 day without continually adding liquid nitrogen to the Dewar. All gases used were purchased from the Matheson Gas Co. and were of the highest purity available, with the exception of methane which was 99.95% pure.

After about 24 h (in the dark) all of the ^{77}Kr has decayed to ^{77}Br, and for the parent–daughter system $^{76}\mathrm{Kr} \rightarrow {}^{76}\mathrm{Br} \rightarrow {}^{76}\mathrm{Se}$, the maximum activity of ^{76}Br is present. At this time the samples were analyzed by using the following procedure. To the frozen contents of the reaction vessel was added a small amount (approximately 0.25 mL) of 90% CH_3OH–10% H_2O saturated with Na_2SO_3 (to reduce all inorganic Br to Br^-). Next, the vessel was warmed and shaken to dissolve the carrier-free quantities of bromide reaction products and unreacted bromine in the CH_3OH–H_2O solution. The vessel was again placed in liquid nitrogen to freeze first the CH_3OH–H_2O mixture, which contained all the bromine activity, and then the hydrocarbon gas on top of it. The vessel was then slowly warmed so the hydrocarbon melted first. At this point the valve was opened to release the gas while the CH_3OH–H_2O mixture remains solid. If the valve were opened while the CH_3OH–H_2O mixture was liquid, the rapid decrease in the pressure above the liquid would cause the reactant gas dissolved in the liquid to buble out, perhaps flushing some volatile bromine compounds (e.g., CH_3Br) from the solution.

After the reactant gas was released, the CH_3OH–H_2O mixture was warmed to melting. In high-pressure samples the dissolved reactant gas could be observed to bubble out, causing the liquid to foam and probably sweep some bromine compounds from the solution. However, the solution was then shaken to redissolve all bromides in the solution, and the procedure was then repeated until all reactant gas was released. With use of this technique no bromides were lost from the vessel during the release of the reactant gas, which was verified by counting the ^{77}Br activity in the vessel before and after the gas was released and by counting the gas which was released. The activity of ^{77}Br before and after was the same, and no ^{77}Br was observed in the gas which was released.

The CH_3OH–H_2O solution was then quickly injected onto three 2-ft Waters Associates Corasil C-18 liquid chromatographic columns ($^3/_8$-in. i.d.) in series. Retention times were determined by using commercially available authentic compounds. They were either injected as purchased and detected by using a refractive index detector or, when solvent fronts of changing composition (and refractive index) made this possible, they were first exchange labeled with $^{77}Br^-$, injected, and detected by using a NaI scintillation crystal (see below). For the first 20 min the mobile phase was 99% water–1% CH_3CN. After that time it was switched automatically by a solvent programmer to 30% CH_3CN–70% water and in some cases to 60% CH_3CN after another time interval. The total flow rate was constant at 2.0 mL/min. Switching to a higher percentage CH_3CN allowed for the elution of the more nonpolar bromides (e.g., butyl bromide) in a much shorter length of time. In addition, dimethylformamide was injected onto the column at the end of the run to elute any remaining activity. While high-pressure liquid chromatography has the disadvantage of incomplete resolution of some organic compounds, the advantages of this method include ability to analyze both inorganic as well as organic components of the radioactive mixture, ease in retrieving separated fractions for later γ-spectroscopic analysis, and absence of possible pyrolytic effects which may occur by using alternative gas chromatographic methods.

The eluant was passed through a stainless-steel loop wrapped around a 2 in. × 2 in. NaI (Tl) scintillation detector which counted the combined ^{77}Br and ^{76}Br activity in each separated component. These counts were collected in a computer system for storage and later analysis. The eluant was collected in fractions and counted on a Ge (Li) γ-ray spectrometer (Ortec Corp., Oak Ridge, TN) in order to determine for each component (peak) the ratio, R, of the activity of ^{77}Br to that of ^{76}Br as detected by the NaI scintillation detector. From R one can calculate for each peak the ^{77}Br and ^{76}Br activities. Then it is possible to sum all of the ^{77}Br and ^{76}Br activities and to express each component as percent ^{77}Br of total ^{77}Br activity and percent ^{76}Br of total ^{76}Br activity.

Table II. Product Yields for Reaction with Solid CH_4

product	% ^{77}Br yield	% ^{76}Br yield	^{76}Br yield/ ^{77}Br yield
CH_3Br	13.8 (38.0)	36.5 (59.3)	2.64 (1.56)
C_2H_5Br	18.9 (52.1)	15.9 (25.8)	0.841 (.495)
c-C_3H_5Br	≲0.1	≲0.1	
C_3H_7Br	2.9 (8.0)	8.1 (13.1)	2.8 (1.6)
C_4H_9Br	0.7 (1.9)	2.6 (4.2)	3.7 (2.2)
$C_5H_{11}Br$	≲0.1	≲0.1	
total organic	36.3	61.6	1.69

Table III. Product Yields for Reaction with Solid C_2H_6

product	% ^{77}Br yield	% ^{76}Br yield	^{76}Br yield/ ^{77}Br yield
CH_3Br	2.8 (6.6)	2.8 (4.0)	1.0 (0.61)
C_2H_5Br	13.2 (30.9)	33.5 (47.3)	2.54 (1.53)
c-C_3H_5Br	0.7 (1.6)	1.2 (1.7)	1.7 (1.1)
C_3H_7Br	18.0 (42.2)	9.4 (13.3)	0.52 (0.32)
C_4H_9Br	5.8 (13.6)	18.2 (25.7)	3.14 (1.89)
$C_5H_{11}Br$	1.2 (2.8)	2.8 (4.0)	2.3 (1.4)
$C_6H_{13}Br$	1.1 (2.6)	3.0 (4.2)	2.7 (1.6)
total organic	42.7	70.8	1.66

Table IV. Product Yields for Reaction with Solid C_3H_8

product	% ^{77}Br yield	% ^{76}Br yield	^{76}Br yield/ ^{77}Br yield
CH_3Br	2.9 (7.4)	4.3 (6.0)	1.5 (0.81)
C_2H_5Br	2.8 (7.2)	3.4 (4.7)	1.2 (0.65)
c-C_3H_5Br	2.0 (5.1)	6.8 (9.5)	3.4 (1.9)
C_3H_7Br	25.4 (65.1)	36.0 (50.2)	1.42 (0.771)
C_4H_9Br	2.5 (6.4)	6.5 (9.1)	2.6 (1.4)
$C_5H_{11}Br$	1.5 (3.8)	5.7 (7.9)	3.8 (2.1)
$C_6H_{13}Br$	1.9 (4.9)	8.0 (11.2)	4.2 (2.3)
total organic	39.0	71.7	1.84

Results

The results for solid-phase reactions at −196 °C for the five hydrocarbons methane, ethane, propane, ethylene, and cyclopropane are given in Tables II–VI. The first number in each of the two columns represents the ^{76}Br and ^{77}Br yields as percent of total activity, and the far right-hand column expresses the ^{76}Br/^{77}Br yield ratios. The numbers in parentheses are yields expressed as percent of the total organic yield; the ^{76}Br/^{77}Br yield ratios for these values are shown in parentheses in the far right hand column. Each value represents the average from two or three experiments. The total organic yields varied from one substrate to another, which may be due in part to chemical differences but also may represent the fact that different amounts of the krypton isotopes may be dissolved in the solid matrix. Thus in the attempted study of solid butane, low total organic yields were observed (approximately 10%). At the freezing point of butane, krypton still has a large vapor pressure, and, at the time the butane freezes, the reaction vial still contains a substantial quantity of undissolved krypton. Low yields (approximately 10%) were also obtained in C_2H_4 solid-phase studies, perhaps because of the fact that C_2H_4 sublimes, which may affect the amount of krypton which becomes dissolved in the solid. Differences in the crystal structure from one frozen gas to another may also cause differences in the total organic yields.[10,11] Expressing product yields as percentages of total organic yields partially circumvents this problem and makes comparison of individual product yields from one substrate system to another straightforward.

---

(10) Horning, E. O.; Willard, J. E. *J. Am. Chem. Soc.* **1957**, *79*, 2429.
(11) Habne, R. M.; Willard, J. E. *J. Phys. Chem.* **1964**, *68*, 2582.

Table V. Product Yields for Reaction with Solid C_2H_4

product	% ^{77}Br yield	% ^{76}Br yield	^{76}Br yield/ ^{77}Br yield
CH_3Br	0.5 (1.5)	0.8 (1.4)	1.6 (0.93)
$C_2H_5Br^a$	15.0 (47.4)	19.9 (35.1)	1.33 (0.74)
c-C_3H_5Br	1.1 (3.4)	2.6 (4.6)	2.4 (1.4)
C_3H_7Br	4.7 (14.4)	4.3 (7.6)	0.91 (0.53)
c-$C_4H_7Br^b$	2.2 (6.7)	3.6 (6.3)	1.6 (0.94)
C_4H_9Br	7.1 (21.7)	20.1 (35.4)	2.83 (1.63)
C_5H_9Br	1.2 (3.7)	3.2 (5.6)	2.7 (1.5)
$C_6H_{13}Br$	0.8 (2.4)	2.2 (3.9)	2.8 (1.6)
total organic	32.7	56.7	1.73

[a] Also contains some C_2H_3Br; see Table VII. [b] Surmised identity since peak bears same relationship to C_4H_9Br as c-C_3H_5Br does to C_3H_7Br.

Table VI. Product Yields for Reaction with Solid c-C_3H_6

product	% ^{77}Br yield	% ^{76}Br yield	^{76}Br yield/ ^{77}Br yield
CH_3Br	0.5 (1.3)	1.2 (2.3)	0.42 (1.8)
C_2H_5Br	11.4 (30.5)	15.4 (29.9)	1.35 (0.980)
c-C_3H_5Br	1.7 (4.5)	2.7 (5.2)	1.6 (1.2)
C_3H_7Br	19.4 (51.9)	23.3 (45.2)	1.20 (0.871)
C_4H_9Br	2.6 (7.0)	5.1 (9.9)	2.0 (1.4)
$C_5H_{11}Br$	1.0 (2.7)	2.0 (3.9)	2.0 (1.4)
$C_6H_{13}Br$	0.7 (1.9)	1.8 (3.5)	2.6 (1.8)
total organic	37.4	51.5	1.38

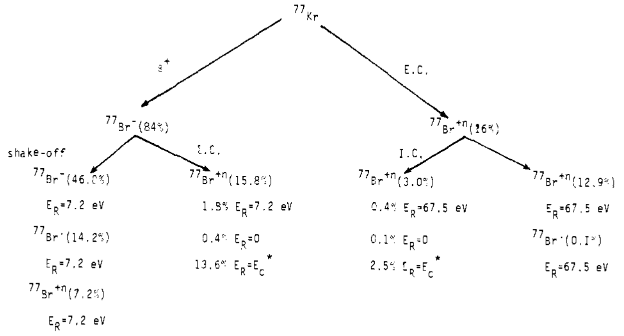
Table VII. Distribution (%) of ^{76}Br and ^{77}Br between Isopropyl and *n*-Propyl Bromide and Ethyl and Ethylene Bromide in the Solid-Phase Studies

	i-C_3H_7Br		*n*-C_3H_7Br		C_2H_3Br		C_2H_5Br	
	^{77}Br	^{76}Br	^{77}Br	^{76}Br	^{77}Br	^{76}Br	^{77}Br	^{76}Br
CH_4	26	13	74	87	(≲0.1)		(~100)	
C_2H_6	83	74	17	26	(≲0.1)		(~100)	
C_3H_8	71	45	29	55	(≲0.1)		(~100)	
C_2H_4	(~100)		(≲0.1)		25	25	75	75
c-C_3H_6	(~100)		(≲0.1)		(≲0.1)		(~100)	

The analytical procedure as described in the Experimental Section did not separate saturated from unsaturated alkyl bromides and only partially separated *i*-C_3H_7Br from *n*-C_3H_7Br. With standard chromatographic conditions, *i*-C_3H_7Br and *n*-C_3H_7Br were sufficiently resolved to make reasonable estimates of the relative contribution of each to the total propyl bromide yield. These results are shown in Table VII as percent of the total propyl bromide yield for the *i*-$C_3H_7{}^{77}Br$/*i*-$C_3H_7{}^{76}Br$ and *n*-$C_3H_7{}^{77}Br$/*n*-$C_3H_7{}^{76}Br$ pairs. Also, under normal chromatographic conditions there was no separation of C_2H_3Br and C_2H_5Br, but with use of a mobile phase of 100% H_2O at 2.0 mL/min for about 2.5 h, they could be separated. With these conditions each substrate system was analyzed to assess the contribution of C_2H_3Br to the C_2H_5Br peak as indicated in Tables II–VI. Only C_2H_4 gave any C_2H_3Br (see Table VII).

Discussion

Before the experimental results are discussed, the importance of highly charged species for both isotopes must be further defined. From the decay scheme of ^{77}Br and internal conversion coefficients for nuclear levels which are converted to a significant extent,[9] one can predict the percent of ^{77}Br atoms which will be charged due to this effect. Shake-off following pure β^+ or EC decay also contributed to the formation of bromonium cations,[12] so the net effect is that 39.0% of all ^{77}Br atoms is positively charged. As shown in Figure 3, the recoil energy of each of these charged fractions differs since high kinetic energies are found with the IC process only when it occurs quickly after β^+ or EC decay. Fast (10^{-10}–10^{-11} s) IC occurs in 2.2% of all ^{77}Br decays,[9] and the remaining ^{77}Br atoms which undergo IC via levels with long ($>10^{-10}$ s) lifetimes are formed with kinetic energies only when chemically combined, because only then will the Coulombic explosion mechanism be operative.[13,14] In Figure 3, we have assumed that of the order of 3% of these atoms will be combined as a result of the original β^+ or EC decay, since approximately 3% is the empirical yield for $CH_3{}^{77}Br$ at low density.[15]



*E_C = kinetic energy which results from internal coulombic forces when the ^{77}Br undergoing I.C. is chemically combined

Figure 3. Charge and kinetic energy spectrum for ^{77}Br as formed from decay of ^{77}Kr.

In the case of ^{76}Br, only a very small fraction of all ^{76}Br atom decays via IC and nearly all IC decays are rapid.[16] We can therefore regard all ^{76}Kr decays as forming ^{76}Br only as the result of EC and with a recoil energy of 7.5 eV (see Table I).

In the solid phase, organic yields are some 10–20 times higher than in the low-pressure gas-phase region[15] and many products are formed from a single substrate molecule (see Tables II–VI). This indicates that caging reactions are predominantly responsible for the observed product distributions. The most important observation in these systems is that the individual product yields are very different for ^{77}Br and ^{76}Br and that the ^{76}Br/^{77}Br yield ratio varies from product to product. This variation in ^{76}Br/^{77}Br yield ratio indicates that the radical environments formed around each isotope are composed of very different proportions of the various organic fragments with which the bromine atom ultimately combines.

One possible explanation for this different radical environment is the fact that the two isotopes have different ranges in the solid media due to the differences in their recoil energies and will be located in different regions of the radical environment formed due to the Auger process. At the low recoil energies of ^{76}Br and ^{77}Br nuclear stopping (as opposed to electronic stopping) is the predominant mechanism by which the atoms are slowed.[17] Expressions for nuclear stopping power[18,19] can be used to predict the range as measured along the pathlength as approximately 15 Å for ^{76}Br, 14 Å (average) for ^{77}Br (β^+), and 135 Å for ^{77}Br (EC). These values represent ranges along the pathlength rather than the projected radial ranges from the site of decay, which is much smaller due to large angle scattering associated with nuclear collisions.[17,19] This will tend to reduce the actual range of the two isotopes. However, the reaction site of the ^{77}Br atom will be located farther from the center of the spherical region of radical formation and so in a region of lower concentration of radicals. Therefore, one would expect, for example, in the CH_4 system less formation of C_2H_5Br in the case of ^{77}Br, whereas the contrary is observed. The same holds for the ethane system where more C_3H_7Br is observed for ^{77}Br, not less. For these reasons, the

---

(12) Krause, M. O.; Carlson, T. A. *Phys. Rev.* **1967**, *158*, 18.

(13) Carlson, T. A.; White, R. M. *J. Chem. Phys.* **1963**, *38*, 2930.

(14) Wexler, S. *J. Chem. Phys.* **1962**, *36*, 1992.

(15) Frost, J. J.; Moerlein, S. M.; Welch, M. J., *J. Am. Chem. Soc.*, following article in this issue.

(16) Paradellis, T.; Houdayer, A.; Mark, S. K. *Yad. Fiz.* **1973**, *A201*, 113.

(17) Bohr, N. *Mat.-Fys. Medd.—K. Dan. Vidensk. Selsk.* **1948**, *18*, No. 8.

(18) Lindhart, J.; Nielson, V.; Scharff, M. *Mat. Fys. Medd. Dan. Vidensk* **1968**, *36*, No. 10.

(19) Lindhart, J. *Proc. R. Soc. London, Ser. A* **1969**, *A311*, 11.

Table VIII. Free-Radical Reactions of Methane

radical	radical-generating reaction	$\Delta H_\mathrm{R}^\circ$,[a] eV	bromination product	$\Delta H_\mathrm{R}^\circ$ brom,[b] eV
CH_3	$CH_4 = CH_3 + H$	4.51 ± 0.04	CH_3Br	1.47 ± 0.04
C_2H_5	$2CH_4 = C_2H_5 + 3H$	9.45 ± 0.04	C_2H_5Br	6.50 ± 0.04
i-C_3H_7	$3CH_4 =$ *i*-$C_3H_7 + 5H$	14.44 ± 0.04	*i*-C_3H_7Br	11.49 ± 0.04
c-C_3H_5	$3CH_4 =$ c-$C_3H_5 + 7H$	20.77 ± 0.04	c-C_3H_5Br	17.95 ± 0.04[c]
t-C_4H_9	$4CH_4 =$ *t*-$C_4H_9 + 7H$	19.34 ± 0.04	*t*-C_4H_9Br	16.43 ± 0.09
neo-C_5H_{11}	$5CH_4 =$ neo-$C_5H_{11} + 9H$	24.54 ± 0.04	neo-$C_5H_{11}Br$	21.51 ± 0.13[c]

[a] Based upon bond dissociation energies in ref 27. [b] Based upon enthalpies of formation in ref 28. [c] Based upon enthalpies of formation in ref 29.

general differences in product distributions are probably not due to differences in ranges for the two isotopes.

A second possibility is the IC decays proceeding through long-lived states of ^{77}Br are giving rise to the differences because when the first activation process due to ^{77}Kr decay occurs, organic incorporations may take place creating a new brominating species. However, only 16.7% of all ^{77}Br atoms decay via this mode, which is much too low to account for the observed organic yields.

From these arguments we come to the conclusion that the difference in recoil energy between ^{76}Br and ^{77}Br is responsible for differences in the product distributions. While the ^{77}Br total organic yields vary from 32% to 42%, only 18.8% + 12.9% = 31.7% of all ^{77}Br atoms are formed in a radiolytic region induced by an Auger process. Thus bromine atoms formed by positron decay (other than those which also undergo IC) must be reacting. When Br^- is eliminated from consideration due to its expected low reactivity,[20] Br· and Br^{n+} formed by shake-off following positron decay are possible reactive species. The reaction of this fraction (14.2% + 7.2% = 21.4%) of ^{77}Br atoms must take place in a radical environment formed due to recoil energy dissipation since the electrons which are shaken off are of very low energy and are not expected to cause much radiolysis of the surrounding medium. For example, in the case of the 14.2% of ^{77}Br atoms which are formed as Br·, the one electron which is shaken off is expected to have an energy on the order of the ionization potential of the atom,[21,22] i.e., only about 10 eV. This case is similar for the 7.2% formed as Br^{n+}, although the energy of the electrons would be slightly higher.

The predominant effect of dissipation of recoil energy is the dislocation of atoms or molecular fragments from their binding sites,[17-19,23-25] that is, bond rupture. These molecular fragments can form stable bromo compounds only after neutralization of the highly charged bromonium cations to at most 1+ or 2+ charge to avoid subsequent Coulombic explosions or decomposition via deposition of charge neutralization energy. Charge exchange Br^{n+} and its environment produces cationic species from the solid substrate, but these must be neutralized by subsequent "cage" reactions and/or rearrangements to avoid a Coulombic barrier to reaction with bromine. Neutralization is expected to occur rapidly in the solid phase and to compete favorably with rearrangement. Consequently, it is possible that the products form from radical–radical reactions and in some cases via radical–molecule or ion–molecule reaction mechanisms involving rearranged substrate molecules. Consideration of thermodynamic parameters applicable to free radical reactions is possible, whereas little data exist for ionic mechanisms. Although correlations between the enthalpies of formation of radicals and the recoil energy of bromine cannot predict activation energies or kinetic rates, they do indicate which products are thermodynamically favored and can eliminate other mechanisms due to excessive endothermicity.

Table VIII shows thermodynamic parameters for the reaction of bromine atoms with free radicals produced from methane molecules.[26] The $\Delta H_\mathrm{R}^\circ$ for radical precursors indicate which radiolytic fragments are able to be formed from bromine recoil energy, while the $\Delta H_\mathrm{R}{}^\circ{}_\mathrm{brom}$ indicate which of the possible radical fragments are thermodynamically preferred for reaction with Br.

The recoil energy of ^{77}Br exceeds the $\Delta H_\mathrm{R}^\circ$ for all radical precursors in methane (C_1–C_6 alkanes), hence production of both CH_3 and C_2H_5 is expected in high yields. Preference for formation of $C_2H_5{}^{77}Br$ is probably related to the greater mass of the C_2H_5 radical, which diffuses out of the reactive cage slower than the smaller CH_3. By contrast, the major product from reaction of ^{76}Br in solid methane is CH_3Br (Table II). This is expected on the basis of low recoil energy of ^{76}Br (7.5 eV), but the yields of two-, three-, and four-carbon ^{76}Br products are difficult to explain on the basis of the thermodynamics of producing such a large number of carbon fragments from a single $^{76}\mathrm{Kr} \rightarrow {}^{76}\mathrm{Br}$ decay. An explanation for these products is that $CH_2{}^+$ generated from the release of H^+ ions during charge-neutralization of $^{76}\mathrm{Br}^{n+}$ is leading to consecutive ion–molecule reactions chains.[30-32]

$$CH_2{}^+ \xrightarrow{CH_4} C_2H_3{}^+ \xrightarrow{CH_4} C_3H_5{}^+ \rightarrow \cdots$$

Subsequent hydride donation by CH_4 would result in long-chain unsaturated compounds in close proximity to the bromine atom, which can undergo additional reaction via homolytic or electrophilic mechanisms depending on the charge of Br. Such a mechanistic path would explain the greater yield of ^{76}Br relative to ^{77}Br in the propyl bromide and butyl bromide products, since ^{76}Br has much greater cationic character (see Figures 1 and 2). That this is a relatively minor effect for ^{77}Br is shown in Table VII, where the percentage of *n*-C_3H_7Br is greater for ^{76}Br than for ^{77}Br. This implies that chain-initiating addition of Br to olefins is less important for the more energetic ^{77}Br and that more $C_3H_7{}^{77}Br$ forms after carbon radicals condense to form *i*-C_3H_7· than in the case of $C_3H_7{}^{76}Br$.

The results for solid ethane and propane (Tables III and IV, respectively) show that there is a tendency for bromine to react with the largest fragment formed from decomposition of the parent compound. While the enthalpy of reaction to form CH_3, C_2H_5, or C_3H_7 from C_3H_8 is approximately the same, the distribution of kinetic energy imparted to the fragment is inversely proportional to the mass of the radical. Hence C_2H_5 predominates in the reactive cage of ethane (or C_3H_7 in propane), and the corresponding bromo compounds are observed in the greatest yields (Tables III and IV). The higher homologues may be produced via generation of unsaturated substrate molecules from charge exchange with Br^{n+}, which proceed to telomerize to form the various C_3–C_6 products. This hypothesis is supported by the high $^{76}\mathrm{Br}/^{77}\mathrm{Br}$ yield ratio for these products, as well as by the close

---

(20) Kashihara, N.; Vietzke, E.; Zellerman, G. *Chem. Phys. Lett.* **1976**, *39*, 316.

(21) Migdal, A. *J. Phys. (Moscow)* **1941**, *4*, 449.

(22) Feinberg, E. L. *J. Phys. (Moscow)* **1941**, *5*, 423.

(23) Seitz, F.; Koehler, J. S. *Solid State Phys.* **1956**, *2*, 307.

(24) Gibson, J. B.; Goland, A. N.; Milgram, N.; Vineyard, G. H. *Phys. Rev.* **1960**, *120*, 1229.

(25) Abedinzadeh, Z.; Radicella, R.; Tanka, K.; Milman, M. *Radiochim. Acta* **1968**, *12*, 4.

(26) Tables of thermodynamic parameters for the substrates C_2H_6, C_3H_8, C_2H_4, and c-C_3H_6 are available upon request.

(27) "Handbook of Chemistry and Physics", 61st ed.; CRC Press: Cleveland, OH, 1980; p F232.

(28) Cox, J. C.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970; p 140.

(29) Benson, S. W.; Cruickshank, F. R.; Golden, D. M., et al. *Chem. Rev.* **1969**, *69*, 279.

(30) Wexler, S.; Jesse, N. *J. Am. Chem. Soc.* **1962**, *84*, 3435.

(31) Field, F. H.; Franklin, J. L.; Munson, M. S. B. *J. Am. Chem. Soc.* **1963**, *85*, 3575.

(32) Sieck, L. W.; Johnson, R. H. *J. Phys. Chem.* **1963**, *67*, 2281.

similarity in product distribution for ethane (Table III) and ethene (Table V). Table VII indicates that these telomer chains may occur before Br addition on the basis of Markovnikov orientation of C_3H_7Br for the ethane and propane systems.

The low product yields for reaction in solid ethene (Table V) may not reflect low reactivity of the nascent bromine but rather failure of the intermediate radical (following Br addition) to abstract hydrogen from neighboring C_2H_4 molecules. The mechanism for C_3H_7Br production probably involves direct recoil dissociation of ethane ($C_2H_4 = 2CH_2$, $\Delta H = 9.06$ eV), which may be assisted through the charge neutralization process. Such single-carbon radical addition to ethene would produce a secondary C_3H_7 radical which could react with Br to give the virtually complete $i\text{-}C_3H_7Br$ results shown in Table VII.

The product yields for reaction of decay-produced bromine with cyclopropane probably involve rearrangement of the substrate to allene rather than fragmentation of the parent compound. The activation energy for the formation of alkyl radical from $c\text{-}C_3H_6$ is ~0.8 eV,[33] so we can expect that rearrangement of $c\text{-}C_3H_6$ to form C_3H_6 should be possible for both ^{76}Br and ^{77}Br. However, the complete yield of $i\text{-}C_3H_7Br$ (Table VII) indicates that it is the rearranged allyl radical which reacts with bromine rather than the anti-Markovinikov addition of Br to allene. The substantial yield of C_2H_5Br may be related to the thermodynamic ease for cyclopropane decomposition to ethene ($2c\text{-}C_3H_6 = 3C_2H_4$, $\Delta H_R° = -2.72 \pm 0.02$ eV), which may further telomerize to give the higher homologues of Table VII.

Conclusion

A method to study the chemical effects of nulear transformations which produce bromine atoms has been described. This method involves the generation of ^{76}Br and ^{77}Br which are formed by the decay of ^{76}Kr and ^{77}Kr, respectively. It was interesting to compare these two bromine isotopes since the energetics and decay modes of each are different, and therefore differences would be expected in their reactivities. The reactions of both bromine isotopes can be studied simultaneously with the use of γ-ray spectrometer since each emits characteristic gamma rays. High-pressure liquid chromatography was applied to the study of these isotopes as an analytical procedure since this method possesses some advantages over the more conventional method of gas chromatography.

In the solid phase at 77 K very different product distributions were observed for the two isotopes. These differences were interpreted in terms of variations in charge states and recoil energy for ^{76}Br and ^{77}Br. Bromine-76 reactions involve combination with unsaturated compounds which result from rearrangement of carbonium ions produced during charge neutralization of bromonium cations. Contrasting are the reactions of ^{77}Br, which result primarily from radicals produced by dissipation of recoil energy in the solid substrate. The differences in the product distributions for the two isotopes are due to the fact that the nature of the reactive cage environment is different when produced as the result of charge neutralization or recoil energy dissipation.

Acknowledgment. We thank the staff of the Washington University who operated the 52-in. cyclotron for their assistance. J. J. F. was supported by NIH MSIP Grant No 5-T05-GM02016.

---

(33) Kerr, J. A.; Smith, A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1969**, 1400.

Reactions of Recoil Bromine Formed by the $^{76,77}Kr \rightarrow ^{76,77}Br$ Systems with Simple Hydrocarbons. Pressure and Additive Effects on Gas-Phase Reactivity[1]

James J. Frost, Stephen M. Moerlein, and Michael J. Welch*[2]

Contribution from the Mallinckrodt Institute of Radiology, Washington University School of Medicine, St. Louis, Missouri 63110. *Received July 31, 1980*

Abstract: Recoil bromine species produced by the systems $^{76,77}Kr \rightarrow ^{76,77}Br$ were reacted with a series of hydrocarbons in the gas phase over the density range 2×10^{-5} to 0.5 g/cm^3. In the region below 100 atm differences in reactivity are related to differences in decay modes and recoil energies. In the low-density methane system an ion-molecule mechanism involving excited CH_4Br^+ is suggested. At higher pressures, the yields are explained in terms of the onset of "caging" reactions due to autoradiation effects. At high percent "inert" moderator, yields increased for CH_4, above those of the pure methane system. Brominating complexes such as $KrBr^+$ and $ArBr^+$ are hypothesized to explain the results.

The influence of charge and kinetic energy on the reactions of bromine atoms produced by nuclear recoil methods have been studied intensively for several decades.[3] The large variety of nuclear processes which are available for the production of bromine atoms often result in bromine atoms with different initial kinetic energies, initial charges, and initial degrees of electronic excitation. On the basis of these differences in the initial state of the bromine atom, in most cases one can expect differences in its chemical reactivity. By correlating such differences with knowledge of the charge, kinetic energy, and electronic state at the time the atom reacts, one can hope to gain insight into the manner in which these variables influence chemical reactions.

This work represents a study of the reactions of two isotopes of bromine, ^{76}Br and ^{77}Br, which are produced by the method of decay-induced activation. The ^{76}Br and ^{77}Br produced in this manner have different kinetic energies and charges and will be shown to display significant differences in chemical reactivity in the gas phase, as has been done for the solid phase.[4]

Experimental Section

The method used in this work for the production and purification of ^{76}Kr and ^{77}Kr has been described previously.[4] The purified, carrier-free ^{76}Kr and ^{77}Kr are Toepler-pumped into reaction vessels, and the other

---

(1) This work was supported in part by NIH Grants HL13851 and HL14147.

(2) To whom correspondence should be addressed.

(3) For review articles and books see: (a) Campbell, I. G. *Adv. Inorg. Chem. Radiochem.* **1963**, *5*, 135. (b) Wolfgang, R. *Prog. React. Kinet.* **1965**, *3*, 97. (c) *Chem. Eff. Nucl. Transform., Proc. Symp.* **1965**. (d) Stocklin, G. "Chemie Heisser Atome"; Verlag Chemie: Weinheim, West Germany, 1969. (e) Urch, D. S. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *8*, 149.

(4) Frost, J. J.; Moerlein, S. M.; Welch, M. J. *J. Am. Chem. Soc.*, preceding article in this issue.

0002-7863/81/1503-4337$01.25/0 © 1981 American Chemical Society