

Failure to Bond Rupture and Nuclear Recoil Following (n, γ) Activation*

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Following the absorption of a thermal neutron by ^{127}I or ^{79}Br , the neutron-binding energy is frequently released in the form of a gamma-ray cascade. As a result of partial cancellation of gamma-ray momenta, a small fraction of the activated halogens will not receive sufficient recoil momentum to rupture from their parent compound. The gas-phase failures to bond rupture following $^{127}\text{I}(n, \gamma)^{128}\text{I}$, and $^{79}\text{Br}(n, \gamma)^{80}\text{Br}$ activation were found experimentally to be: CH_3I —1.09, CD_3I —0.68, CF_3I —0.12, $\text{C}_2\text{H}_5\text{I}$ —0.082, $n\text{-C}_3\text{H}_7\text{I}$ —0.66, $i\text{-C}_3\text{H}_7\text{I}$ —0.30, CH_3Br —0.25, CD_3Br —0.20, CH_2Br_2 —0.12, CF_3Br —0.11, CF_2Br_2 —0.093, CHClBr_2 —0.087, CCl_2Br —0.066, CHBr_3 —0.05, CBr_4 —0.03, $\text{C}_2\text{H}_5\text{Br}$ —0.33, and $1,1\text{-C}_2\text{H}_4\text{Br}_2$ —0.17%. These data are correlated with the calculated recoil energies required for bond rupture (preceding article). Using as a basis the distribution of net gamma-ray energies calculated by the random-walk method for the $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$ process, the kinetic-energy distributions of the dissociated ^{128}I or ^{80}Br are approximated. These data suggest that the extent of hot-atom reaction of ^{128}I or ^{80}Br with CH_4 should not depend upon the parent molecule from which the activated halogen dissociates.

INTRODUCTION

IF an isolated atom absorbs a thermal neutron and the neutron binding energy is released as a single gamma ray, then, as a result of conservation of momentum, the atom will receive a recoil kinetic energy of¹

$$E_T = 537 E_\gamma^2 / m_N, \quad (1)$$

where E_γ is the energy (in Mev) of the gamma quantum, m_N is the mass (in amu), and E_T is the recoil energy (in ev) of the activated atom. Such energy is usually greatly in excess of thermal energies. For example, the neutron-binding energy associated with the $^{127}\text{I}(n, \gamma)^{128}\text{I}$ process is 6.6 Mev; an isolated ^{128}I atom releasing this energy as a single gamma ray would acquire 182 ev of kinetic energy.

If the atom which undergoes an (n, γ) reaction is bound chemically, it is not immediately obvious how the gamma-ray recoil is transferred to the atom and the molecule. The observations of Szilard, Chalmers, and subsequent experimenters have shown that most of the atoms activated by the (n, γ) process rupture from their parent compound. This indicates that at least a fraction of the gamma-recoil momentum must be deposited in the bond joining the activated atom to the molecule. For a given isotope, the gamma-ray momentum required for bond rupture should depend not only on the bond energy but also on the chemical radical to which the activated atom is bound.

Suess² calculated that, for a diatomic molecule, the

internal energy E_i will be increased by

$$\Delta E_i = (537 E_\gamma^2 / m_N) [(\Sigma m_i - m_N) / \Sigma m_i], \quad (2)$$

where Σm_i is the molecular weight of the molecule.

In the preceding article,³ a method is proposed for calculating the increase in internal energy of a polyatomic molecule.

If a single gamma ray, of the order of 6 Mev energy, is emitted by an atom it would be expected that the activated atom would always rupture from its parent compound. The only exception would be, perhaps, the case where the activated atom was bonded to an atom of small atomic weight, as in the hydrogen halides, for example. However, indirect experimental evidence⁴ indicated that in the (n, γ) activation of gaseous $\text{C}_2\text{H}_5\text{I}$, of the order of 1% of the ^{128}I did not rupture from the parent molecule.

Such failure to bond rupture can be explained. In (n, γ) activation, and particularly in the activation of the halogens, the neutron-binding energy is released most frequently not as a single gamma quantum, but as a gamma-ray cascade. Because of partial cancellation of gamma-ray momenta, some of the atoms could receive a net-recoil momentum which is less than that required for bond rupture.

If the complete neutron-capture gamma-ray cascade spectrum is known, and if there are no angular correlations between the gamma rays, then, using the method of random walks,⁵ the net gamma-ray momentum probabilities can be calculated. [Such a calculation has been performed for the $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$ process.⁵] In addition, if the net gamma-ray momentum required for bond rupture can be calculated, then it is possible to predict the percent of the activated atoms which fail

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¹See, for example: R. R. Edwards and T. H. Davies, *Nucleonics* **2**, 44 (1948), or A. C. Wahl and N. A. Bonner, *Radioactivity Applied to Chemistry* (John Wiley & Sons, Inc., New York, 1951), p. 511.

²H. Suess, *Z. physik Chem.* **B45**, 312 (1940).

³C. Hsiung and A. A. Gordus, *J. Chem. Phys.* **36**, 947 (1962), preceding article.

⁴A. A. Gordus and J. E. Willard, *J. Am. Chem. Soc.* **79**, 4609 (1957).

⁵C. Hsiung, H. Hsiung, and A. A. Gordus, *J. Chem. Phys.* **34**, 535 (1961).

to rupture from their parent compound. The purpose of this study was to determine experimentally the extent of the failure to bond rupture of ^{128}I and ^{80}Br when in the form of alkyl halides. In addition, it was desired to evaluate, if possible, the proposed mathematical model³ describing the transfer of momentum from the gamma rays to the internal modes of the molecules.

EXPERIMENTAL

Quartz bulblets, of 4–5-ml size, were filled with about 10–15 mm (if possible) of an alkyl halide and about 700 mm of NO. Generally, 0.1-mm I_2 (or Br_2) was also added. The organic bromides were purified by stirring with concentrated H_2SO_4 followed by washing with water, drying, and distillation. The organic iodides were passed through a silica gel-alumina column and then distilled. The samples were packed in Lusteroid rabbit capsules, thus shielding them from light; if they were not to be irradiated within a few hours, they were stored in a refrigerator.

The samples were irradiated in the University of Michigan megawatt reactor for about 30–45 sec at a thermal neutron flux of $1.5 \times 10^{12} \text{n/cm}^2\text{-sec}$ and an accompanying gamma-radiation flux of 8000 r/min.

The nitric oxide served three purposes. (1) It is an efficient radical scavenger and thus, should serve to suppress radiation-induced reactions. (2) It should react easily with the ^{80}Br atoms dissociating from the alkyl bromides thus preventing the ^{80}Br from returning to organic combination. In the case of the ^{128}I , it has been shown⁶ that NO is an effective moderator for the $^{128}\text{I} + \text{CH}_4$ reaction, the moderation being due, perhaps, to the fact that NO can effectively neutralize I^+ ions. (3) Large amounts of NO, or, for that matter, any molecular additive, will serve to reduce the kinetic energy of the recoiling halogen atoms before they collide with an organic-halide molecule and thus assist in preventing these atoms from reforming organic compounds.

Since it was expected that the extent of failure to bond rupture would be 1% or less, it was of utmost importance to be able to separate completely the dissociated halogen from the organic halide. To accomplish this, the following procedure was used.

After irradiation, the bulbs were broken in a separatory funnel beneath an aqueous solution of Na_2SO_3 ; chloroform containing a small amount of I_2 was added immediately and the mixture shaken to extract organic halides. The two phases were each counted for a period of about 20 min and, after correcting for coincidence-loss and density effects, the percent of the total activity found in the organic phase was calculated.

The extraction procedure was evaluated by irradiating mixtures of $\text{NO} + \text{I}_2$ and $\text{NO} + \text{Br}_2$ and determining the percent activity found in the organic phase. The results were approximately 0.01% for ^{128}I and 0.004% for ^{80}Br . Thus, any observed organic activity greater

TABLE I. Failure to bond rupture.

Molecule	Percent halogen found as organic	Average ^a
CH_3Br	0.23, 0.29, 0.27, 0.22, 0.25, 0.23, 0.262, 0.25, 0.232	0.25 ± 0.01
CD_3Br	0.28, 0.26, 0.22, 0.16, 0.16, 0.16, 0.17, 0.18	0.20 ± 0.02
CH_2Br_2	0.150, 0.208, 0.195, 0.160, 0.060, 0.130, 0.072, 0.079, 0.162, 0.160, 0.100, 0.172, 0.150, 0.202, 0.020, 0.014, 0.120, 0.093, 0.080, 0.097, 0.130, 0.091, 0.093, 0.103, 0.092, 0.046	0.115 ± 0.010
CF_3Br	0.090, 0.110, 0.100, 0.098, 0.099, 0.093, 0.120, 0.115, 0.123	0.105 ± 0.004
CF_2Br_2	0.105, 0.112, 0.086, 0.088, 0.082, 0.091, 0.089	0.093 ± 0.004
CHClBr_2	0.090, 0.092, 0.109, 0.083, 0.091, 0.068, 0.075	0.087 ± 0.005
CCl_3Br	0.057, 0.072, 0.051, 0.062, 0.079, 0.080, 0.061	0.066 ± 0.004
CHBr_3	0.089, 0.030, 0.044, 0.028	0.048 ± 0.013
CBr_4	0.032, 0.051, 0.034, 0.044, 0.026	0.031 ± 0.006
$\text{C}_2\text{H}_5\text{Br}$	0.31, 0.28, 0.41, 0.38, 0.31, 0.26, 0.45, 0.21	0.33 ± 0.03
$1,1\text{-C}_2\text{H}_4\text{Br}_2$	0.157, 0.175, 0.151, 0.183, 0.200	0.173 ± 0.009
CH_3I	1.10, 1.10, 0.99, 1.00, 1.14, 1.05, 1.24	1.09 ± 0.03
CD_3I	1.03, 1.02, 1.12, 0.45, 0.56, 0.94, 0.65, 0.56, 0.52, 0.43, 0.23, 0.45, 0.71, 0.99, 0.56, 0.65	0.68 ± 0.06
CF_3I	0.176, 0.158, 0.118, 0.112, 0.083, 0.091	0.12 ± 0.02
CH_2I_2	0.06, 0.07, 0.08, 0.056, 0.07, 0.070	0.068 ± 0.004
$\text{C}_2\text{H}_5\text{I}$	0.87, 0.90, 0.82, 0.76, 0.71, 0.82, 0.75, 1.01, 1.05, 0.57, 0.96, 0.64	0.82 ± 0.04
$n\text{-C}_3\text{H}_7\text{I}$	0.81, 0.84, 0.72, 0.62, 0.86, 0.85, 0.54, 0.58, 0.48, 0.44, 0.55	0.66 ± 0.05
$i\text{-C}_3\text{H}_7\text{I}$	0.14, 0.46, 0.26, 0.32, 0.34	0.30 ± 0.05

^a Uncertainty is the standard deviation of the mean.

than these values is not due to inorganic halogen dissolved in the organic phase.

RESULTS

Listed in Table I are the observed values of the percent of the halogen activity found in the organic phase. The uncertainty is calculated in terms of the standard deviation of the mean.

Let us assume that the ^{128}I or ^{80}Br splits from a mole-

⁶ E. P. Rack and A. A. Gordus, *J. Chem. Phys.* **34**, 1855 (1961).

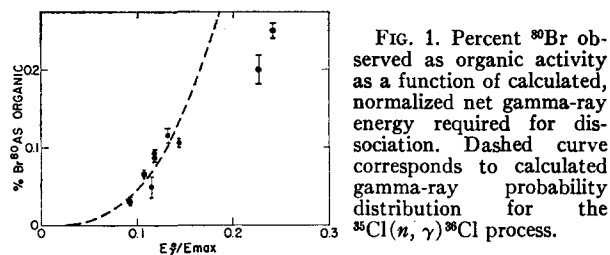


FIG. 1. Percent ^{80}Br observed as organic activity as a function of calculated, normalized net gamma-ray energy required for dissociation. Dashed curve corresponds to calculated gamma-ray probability distribution for the $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$ process.

cule only if it receives a net gamma-recoil momentum sufficient to cause carbon-halogen bond rupture. If this be so, then for a series of molecules, a plot of the percent failure to bond rupture vs the calculated net gamma-ray energy required for bond rupture³ should be identical with a plot of the gamma-ray energy probability vs the net gamma-ray energy.

Since, for these isotopes, the neutron-capture gamma-ray data are inadequate to permit calculating the probabilities, the latter plot cannot be obtained. However, the general shape of the probability curve will, perhaps, be similar to that calculated for the $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$ process.⁵

Presented in Figs. 1 and 2 are the observed percent ^{128}I or ^{80}Br as organic as a function of the fractional gamma-ray energy, $E_\gamma^\circ/E_{\text{max}}$, where $E_\gamma^\circ = (E_T^\circ m_N/537)^{1/2}$, and is the net gamma-ray energy necessary for bond rupture and E_{max} is the neutron-binding energy and equals 6.6 Mev for ^{128}I and 7.3 Mev for ^{80}Br . The dashed curve is the lower-energy portion of the probability vs $E_\gamma^\circ/8.5$ Mev curve for the $^{35}\text{Cl}(n, \gamma)^{36}\text{Cl}$ process. This curve differs slightly from that presented in reference 5 in that recent data⁷ are included in the random-walk calculation.

DISCUSSION

The data presented in Figs. 1 and 2 appear to describe a function characteristic of the energy distribution associated with (n, γ) activation. However, there is no assurance that the E_γ° energies ascribed to the compounds actually correspond to the net gamma-ray energies required for dissociation. This is due to the fact that the formation of ionized or electronically excited halogen is not taken into account. It is known⁸ that at least 18% of ^{80}Br and 50% of ^{128}I formed by (n, γ) activation is positively charged. Such positive charge probably results from the internal conversion of low-energy gamma-rays resulting from cascade-gamma emission.

If a positively charged alkyl-halide molecule is produced, two possible modes of dissociation are $\text{RX}^+ \rightarrow \text{R} + \text{X}^+$ and $\text{RX}^+ \rightarrow \text{R}^+ + \text{X}$. For most alkyl halides, the first process requires the larger amount of energy. If the energy imparted to the halogen is less than that required for the first process, but greater than that re-

quired for the second, then the molecule could remain intact until internal electronic rearrangement occurs. The value of E_γ° required for bond rupture of the positively charged molecule differs from that required for the neutral molecule. For example, $E_\gamma^\circ = 2.77$ Mev for $\text{CH}_3\text{I}^+ \rightarrow \text{CH}_3^+ + \text{I}$ and 2.55 Mev for neutral CH_3I . For $\text{CH}_3\text{Br}^+ \rightarrow \text{CH}_3^+ + \text{Br}$ and CH_3Br , $E_\gamma^\circ = 1.57$ and 1.76 Mev, respectively. Unfortunately, the ionization potential of many of the radicals are not available. Thus, we cannot determine whether the data would approximate a smoother curve if ionization effects were taken into account.

For gamma-cascade emission involving, perhaps, more than three or four gamma-ray quanta another problem arises. It is possible, in such cascade processes, that molecular dissociation occurs before all cascade gamma-rays are emitted. In order to determine the importance of this effect it is necessary to have knowledge of the lifetimes of intermediate nuclear states. Such information is not available, although it can be estimated⁹ that the lifetimes may be of the order of 10^{-15} to 10^{-14} sec.

Since vibrational times are of the order of 10^{-14} sec, the number of gamma rays effecting dissociation may be less than the total number of gamma rays emitted by the nucleus. As a result, the gamma-ray energy-probability distribution which must be evaluated would differ from that calculated for the complete cascade processes, although this distribution would again represent a smooth rising curve. However, if, because of the differences in vibrational times, the number of gamma rays effecting dissociation vary from compound to compound, separate distribution curves would be required for each molecule and the experimental failure to bond-rupture data would not necessarily be expected to approximate a smooth rising curve.

From the above discussion it is apparent that it is not possible to calculate unambiguously either the gamma-ray recoil energy necessary for bond rupture or the recoil-energy distribution associated with the atoms prior to dissociation.

Higher Alkyl Halides

Because of the assumption that the space velocities of the nonrecoiling atoms are the same,³ it is not surpris-

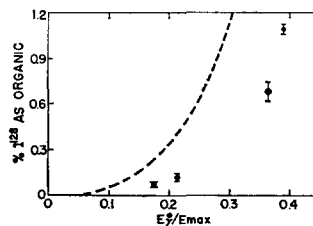


FIG. 2. Refer to Fig. 1. Data are for ^{128}I rupture.

⁷ L. V. Groshev, A. M. Demidov, V. N. Lutsenko, and V. I. Pelekhov, *Atlas of Gamma-Ray Spectra from Radiative Capture of Thermal Neutrons* (Pergamon Press, London, 1959), pp. 48-49.

⁸ S. Wexler and T. H. Davies, *J. Chem. Phys.* **20**, 1688 (1952).

⁹ (a) K. Siegbahn, *Beta and Gamma-Ray Spectroscopy* (Interscience Publishers Inc., New York, 1955), p. 815. (b) *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 8-96.

ing that the data for alkyl halides containing more than one carbon atom do not approximate the same curve as that for the methyl halides. The greater the number of bonds separating an atom in the molecule from the atom receiving the recoil, the less affected will be the non-recoiling atoms, although some of the energy could be deposited in the C—C bond. If it were possible to correct for this effect, the calculated E_{γ}° values would be numerically larger and the data for C_2H_5I , $n-C_3H_7I$, $i-C_3H_7I$, C_2H_5Br , and 1,1- $C_2H_4Br_2$ would probably be more in accord with the data for the methyl halides.

^{36}Cl Recoil

Lacking any other means of comparison, the normalized, calculated $^{35}Cl(n, \gamma)^{36}Cl$ gamma-ray probability curve was also plotted in Figs. 1 and 2. There is no reason to expect the ^{80}Br and ^{128}I data to be in agreement with the ^{36}Cl curve. This calculated curve serves only to indicate the general shape of the probability distribution curve associated with a gamma-recoil process which involves fairly complex gamma-ray cascades. However, the fact that the experimental data do approximate a smooth rising curve similar to that of ^{36}Cl would suggest that the (n, γ) failure to bond rupture is due to partial cancellation of gamma-ray momenta.

DIATOMIC MOLECULES

The gamma-ray recoil energy E_{γ}° required for bond rupture of a diatomic molecule may be calculated exactly according to Eq. (2) since $\Delta E_i = E_{BN}$, the bond-dissociation energy. For $^{80}Br-Br$, $E_{\gamma}^{\circ}/E_{max} = 0.106$; for $^{128}I-I$, the value is 0.095. Referring to Figs. 1 and 2, it is seen that the expected extents of failure to bond-rupture would be approximately 0.05 and 0.02%, respectively. For the hydrogen halides, $E_{\gamma}^{\circ}/E_{max}$ would be much greater than that included in the range of data given in Figs. 1 and 2.

ENERGY DISTRIBUTION

In studies of chemical reactions activated by (n, γ) processes, the chemical reactivity of the activated atoms is frequently found to result from the large translational kinetic energies imparted to the atoms by the neutron-capture gamma rays. It is possible to calculate the energies associated with the recoiling activated atom, the radical to which it was bonded, and the internal energy of the radical.³

Data of Fig. 1 were extrapolated to 100% so that the curve had the same shape as that for the $^{35}Cl(n, \gamma)^{36}Cl$ process.⁵ To determine the probability distribution $P(E_N)$ of the bromine atoms which rupture from their parent compound (99.75% of the ^{80}Br for CH_3Br and 99.97% for CBr_4), it was necessary to correct the above extrapolated curve $P(E_{\gamma})$ for the failure to bond rupture portion $P(E_{\gamma}^{\circ})$ of the curve. Thus,

$$P(E_N) = [P(E_{\gamma}) - P(E_{\gamma}^{\circ})] / [1 - P(E_{\gamma}^{\circ})]. \quad (3)$$

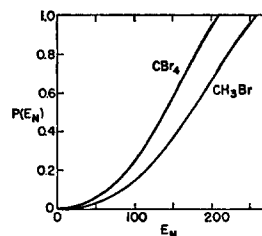


FIG. 3. Probability distribution of dissociated ^{80}Br recoil energies. ^{80}Br source compounds: CH_3Br and CBr_4 .

$P(E_N)$ is presented in Fig. 3 plotted as a function of the translational recoil energy of the dissociated bromine atoms, the values of E_N having been calculated according to Eq. (50) of reference 3.

Preliminary calculations¹⁰ indicate that for $Br + CH_4 \rightarrow CH_3Br + H$ to occur, the Br atoms must possess between approximately 8 and 17 ev of translational kinetic energy. As indicated in Fig. 3, greater than 99% of the ^{80}Br atoms which rupture from CH_3Br or CBr_4 possess greater than 17 ev of translational kinetic energy. As a result, ^{80}Br atoms originally bonded to either of these two compounds would be able to react with CH_4 with equal probability since, in both cases, greater than 99% of the ^{80}Br atoms possess energy in excess of that required for reaction. The compounds, CH_3Br and CBr_4 were chosen for this calculation since they are representative of the two extremes of the type of simple alkyl halides which might be used as ^{80}Br sources.

Hydrogen bromide, however, is unique in that it would be expected that about 85% of the ^{80}Br would fail to undergo bond rupture.¹¹ As a result, most of the energetic ^{80}Br species which collide with CH_4 are in the form of HBr . The energy range required for the reaction of $HBr + CH_4$ to yield CH_3Br undoubtedly differs from the energy range required for simple hydrogen displacement. Thus, the use of HBr as a source of ^{80}Br in gaseous CH_4 systems could result in a percent CH_3Br formation which differs from the 13.3% found¹² in $Br_2 + CH_4$ or alkyl bromide + CH_4 systems.¹³ We are also calculating the energy requirement of the $HBr + CH_4$ reaction.

Reaction of ^{128}I with CH_4 to yield CH_3I would also require ^{128}I translational kinetic energies of the order of 17–21 ev. Therefore, as in the $^{80}Br + CH_4$ reaction, the extent of hot reaction of ^{128}I with CH_4 should be the same irrespective of the alkyl iodide used as the source of ^{128}I .

¹⁰C. Hsiung and A. A. Gordus (unpublished data).

¹¹This value was determined from the extrapolated $P(E_{\gamma})$ curve.

¹²E. P. Rack and A. A. Gordus, *J. Phys. Chem.* **65**, 944 (1961).

¹³A value of 41% ^{80}Br as organic has been reported for the $HBr + CH_4$ system.⁴ We are repeating these experiments and preliminary data indicate the yield is approximately 10%. The difference could be due to the lower gamma-radiation doses in the recent experiments.