Momentum Transfer to an Atom in a Molecule: Internal Excitation and Bond Dissociation*

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An atom will dissociate from a compound if the atom receives a recoil momentum greater than some average value Q^0. Considering a polyatomic molecule as composed of point-mass atoms, there is derived an equation which relates Q^0 to the bond energy, bond angles and distances, and masses of the atoms in the molecule. The minimum net recoil energy required for bond rupture, the kinetic energy of the recoiling radicals, and the internal energy of the radical originally bonded to the activated atom are calculated for a series of simple alkyl halides.

INTRODUCTION

MOMENTUM transfer to an isolated atom is a simple problem in classical mechanics. However, if the atom which receives the impulse is bound chemically, it is not immediately obvious how the recoil energy becomes distributed among the various internal energy modes of the molecule.

For a diatomic molecule, Suess[1] calculated that the internal energy E_i will be increased by

$$\Delta E_i = E_T \left(\sum m_i - m_N \right) / \sum m_i, \qquad (1)$$

where m_N is the atomic weight of the atom receiving the impulse, $\sum m_i$ is the molecular weight of the diatomic molecule, and E_T is the recoil energy acquired by the atom. For gamma-ray recoil,[2] $E_T = (537 E_\gamma^2)/m_N$, where E_T is in units of ev, m_N in amu, and the gamma-ray energy E_γ in Mev.

Steinwedel and Jensen[3] calculated the fractional distribution of the internal energy between the vibrational and rotational modes of a diatomic molecule. In addition, they considered a quantum-mechanical approach to the problem.

Recently, Svoboda[4] discussed the relationship between rotational excitation and the bond dissociation energy. Wolfsberg[5] also included such an effect in his quantum-mechanical evaluation of the beta-decay recoil-excitation of ^{14}C labeled ethane.

To calculate the recoil energy required for chemical bond rupture in a polyatomic molecule it is possible to utilize a quantum-mechanical approach. However,

because of the uncertainties and assumptions associated with such derivations, the calculated value would be considered as only a very rough approximation.

We have considered the problem of recoil momentum activation of polyatomic molecules in terms of a mechanical model. The model which we propose involves only a small number of well-defined assumptions, and these assumptions, at least for the simpler molecules, may not invalidate the results.

THE MODEL

Consider a molecule as consisting of a group of point masses, the atoms linked together by springs. The molecule, therefore, is not rigid and the atoms in the molecule may undergo independent constrained motions in addition to the translational and rotational motions of the molecule. For a molecule composed of N atoms, $3N$ coordinates will be required to describe the molecule in detail. This can be achieved by first defining a set of coordinates $\mathbf{r}(x, y, z)$ with the center of gravity of the molecule G as the origin. The coordinates of the center of gravity of the molecule are $\mathbf{R}(X, Y, Z)$ and the translational motion of the center of gravity of the molecule is $\dot{\mathbf{R}}(\dot{X}, \dot{Y}, \dot{Z})$. The orientation of the molecule in space is usually represented by $\Theta(\theta, \phi, \chi)$ and, thus $\dot{\Theta}$ or ω is the angular motion of the molecule about its center of gravity. In addition, the relative positions of the atoms in the molecule can be described as $\mathbf{r}_i(x_i, y_i, z_i)$ $(i = 1$ to $N)$ thus resulting in $3N-6$ independent coordinates. Although the positions $\mathbf{r}_i$ describe $3N$ coordinates, not all are independent since (1) the choice of the origin as the center of gravity results in

$$\sum m_i \mathbf{r}_i = 0 \qquad (2)$$

and (2) the translation and rotation of the molecule has been described by the translation and rotation of the (x, y, z) coordinates, i.e., $\dot{\mathbf{R}}$ and ω. Thus, there should be no net angular momentum with respect to the (x, y, z) coordinates. As a result,

$$\sum m_i \mathbf{a}_i \times \mathbf{v}_i = 0, \qquad (3)$$

where $\mathbf{a}_i$ is the equilibrium position of the ith atom and $\mathbf{v}_i$ is the vibrational velocity of the ith atom with respect to the molecule.

[1] H. Suess, Z. physik. Chem. **B45**, 312 (1940).
[2] See, 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.
[3] H. Steinwedel and J. H. D. Jensen, Naturforsch. **A2**, 195 (1947).
[4] K. Svoboda, Zhur. Neorg. Khim. **3**, 187 (1958); U. S. Atomic Energy Comm. Nuclear Sci. Abstr. **13**, 10954 (1959).
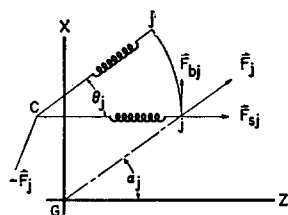[5] M. Wolfsberg, J. Chem. Phys. **24**, 24 (1956).

FIG. 1. Centrifugal force effecting the C—j bond.

When the framework (X, Y, Z) moves at a velocity $\dot{\mathbf{R}}$ and rotates at an angular velocity ω and the atoms simultaneously vibrate around their equilibrium positions $\mathbf{a}_i$ at velocities $\mathbf{v}_i$ then, the space velocity of the ith atom $\mathbf{S}_i$ is

$$\mathbf{S}_i = \dot{\mathbf{R}} + \omega \times \mathbf{r}_i + \mathbf{v}_i.$$

Hence, the total energy of the molecule is

$$E_T = \tfrac{1}{2}\sum m_i(\dot{\mathbf{R}} + \omega \times \mathbf{r}_i + \mathbf{v}_i)^2 + V(\mathbf{r}_i). \quad (4)$$

Since $\dot{\mathbf{r}}_i = \omega \times \mathbf{r}_i + \mathbf{v}_i$ and $\sum m_i \mathbf{r}_i = 0$, it can be shown that

$$\sum m_i \mathbf{v}_i = 0. \quad (5)$$

Using Eqs. (2), (3), and (5), the total energy of the system, Eq. (4), is

$$E_T = \tfrac{1}{2}\sum m_i \dot{R}^2 + \tfrac{1}{2}\sum m_i(\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i)$$
$$+ \tfrac{1}{2}\sum m_i v_i^2 + \omega \cdot \sum m_i(\varrho_i \times \mathbf{v}_i) + V(\mathbf{r}_i), \quad (6)$$

where $\varrho_i = \mathbf{r}_i - \mathbf{a}_i$ is the displacement of the ith atom and $V(\mathbf{r}_i)$ is the potential energy of the molecule.

The first term on the right-hand side of Eq. (6) is the translational energy of the molecule, the second term is the rotational energy, the third term is the vibrational energy, the fourth term is the rotational and vibrational coupling, and the last term is the potential energy of the molecule.

On the average, ϱ_i approaches zero; hence, the internal energy may be approximated by

$$E_{\text{int}} = \tfrac{1}{2}\sum m_i(\omega \times \mathbf{a}_i) \cdot (\omega \times \mathbf{a}_i) + \tfrac{1}{2}\sum m_i v_i^2 + V(\mathbf{a}_i). \quad (7)$$

If an atom in the molecule suddenly experiences a mechanical recoil and if the recoil energy is very large compared to the thermal motion of the molecule, then the total energy increase is

$$\Delta E_T = \tfrac{1}{2}\dot{R}^2\sum m_i + \tfrac{1}{2}\sum m_i(\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i)$$
$$+ \tfrac{1}{2}\sum m_i v_i^2 + V(\mathbf{r}_i) - V(\mathbf{a}_i). \quad (8)$$

The total internal-energy increase is

$$\Delta E_{\text{int}} = \tfrac{1}{2}\sum m_i(\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) + \tfrac{1}{2}\sum m_i v_i^2$$
$$+ V(\mathbf{r}_i) - V(\mathbf{a}_i). \quad (9)$$

Vibrational and Rotational Energy Separation

Let us now examine the potential-energy change $[V(\mathbf{r}_i) - V(\mathbf{a}_i)]$. This change can result from both the vibrational and rotational motions. The vibrational

effect on the potential energy is obvious. The rotational effect on the potential energy can be described as follows. When a molecule is rotating about its center of gravity, centrifugal forces develop stresses in the chemical bonds and, consequently, the bonds are stretched inelastically from their original equilibrium positions $\mathbf{a}_i$ to new equilibrium positions $\mathbf{b}_i$. This results in a rotational potential-energy change of $[V(\mathbf{b}_i) - V(\mathbf{a}_i)]$. The total potential energy change may be rewritten as

$$[V(\mathbf{r}_i) - V(\mathbf{b}_i)] + [V(\mathbf{b}_i) - V(\mathbf{a}_i)],$$

where $[V(\mathbf{r}_i) - V(\mathbf{b}_i)]$ is, therefore, the vibrational potential-energy change. The total internal-energy change ΔE_{int} can be divided into two parts: that resulting from the rotational-energy change ΔE_r and that resulting from the vibrational-energy change ΔE_v, where

$$\Delta E_r = \tfrac{1}{2}\sum m_i(\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) + V(\mathbf{b}_i) - V(\mathbf{a}_i) \quad (10)$$

and

$$\Delta E_v = \tfrac{1}{2}\sum m_i v_i^2 + V(\mathbf{r}_i) - V(\mathbf{b}_i). \quad (11)$$

Assuming that the atoms vibrate as simple harmonic oscillators around their equilibrium positions $\mathbf{b}_i$ the vibrational-energy change becomes

$$\Delta E_v = \tfrac{1}{2}\sum m_i v_{0i}^2, \quad (12)$$

where $\mathbf{v}_{0i}$ is the vibrational velocity of the ith atom at its equilibrium location $\mathbf{b}_i$.

Momentum Excitation in Each Bond

Equations (10) and (12) represent the total vibrational- and rotational-energy changes due to an impulse Q received by an atom N. Although this sudden impulse Q will excite principally those bonds which link atom N to the remainder of the molecule; it will also cause some excitation in the other bonds in the molecule. In order to be able to calculate the impulse required to rupture a particular bond, it is necessary to express ΔE_r and ΔE_v as sums of the energy changes in each bond. The resulting expressions will depend upon the molecular configurations.

Let us consider a molecule which consists of a center atom C and $(i-1)$ remaining atoms $[1, 2, \cdots, j, \cdots (i-1)]$ which are joined only to atom C. (Typical examples of such compounds are: CH_3Br, where the Br receives the impulse; PCl_3, where the Cl receives the impulse; CH_3CH_2Br, where the Br receives the impulse, and the CH_3 is considered as a point mass. If the carbon in a compound such as CH_3Br receives the impulse, a slight modification of the final result is needed.) We define the bond which connects atoms C and j as j, and we define the vibrational and rotational-induced energy changes associated with this bond as ΔE_{vj} and ΔE_{rj}, respectively.

Vibrational-Energy Contribution

Using Eqs. (5) and (12), the vibrational-energy contribution is found to be

$$\Delta E_v = \sum_{j=1}^{i-1}\Delta E_{vj} = \frac{1}{2}\sum_{j=1}^{i-1} m_j \mathbf{v}_{0j} \cdot (\mathbf{v}_{0j} - \mathbf{v}_{0C}). \quad (13)$$

Hence, the vibrational-energy change in bond j is

$$\Delta E_{vj} = \frac{1}{2}m_j \mathbf{v}_{0j} \cdot (\mathbf{v}_{0j} - \mathbf{v}_{0C}). \quad (14)$$

Rotational-Energy Contribution

The rotational-energy change is separated on the basis that the rotational excitation of the chemical bonds is due to the centrifugal stresses developed in the bonds.

The centrifugal forces associated with atoms j and C are $\mathbf{F}_j = m_j \omega^2 \mathbf{r}_j$ and $\mathbf{F}_C = m_C \omega^2 \mathbf{r}_C$; however, $\mathbf{F}_C = -\sum_j \mathbf{F}_j$. Hence, the centrifugal force can be resolved into $-\mathbf{F}_j$ components ($j=1$ to $j=i-1$). The stress in bond j will be due to the centrifugal force $\mathbf{F}_j$ on the jth atom and a portion of the centrifugal force of the atom C, $-\mathbf{F}_j$. Depicted in Fig. 1 are the forces acting on the bond j, where G is the center of gravity and α_j is the angle between Gj and Cj.

The vector $\mathbf{F}_j$ is next resolved into two components: F_{sj} is in the direction of the bond j and will cause a stretching vibration of the bond; F_{bj} is perpendicular to the bond j and will cause a bending vibration in the bond. Using a simple valence-force approximation for the potential, we have

$$F_{sj} = 2F_j \cos\alpha_j = k_{sj}\delta_{sj} \quad (15)$$

and

$$F_{bj} = 2F_j \sin\alpha_j = k_{bj}\delta_{bj}, \quad (16)$$

where k_{sj} is the stretching-force constant, k_{bj} the bending-force constant, δ_{sj} is the elongation of the bond j due to the stretching force F_{sj}, and $\delta_{bj} = |\mathbf{b}_j - \mathbf{b}_C| \theta_j$, where θ_j is the angle through which the bond is deflected due to F_{bj}.

The energy deposited in the bond due to stretching is

$$E_{sj} = 2m_j^2 r_j^2 \omega^4 \cos^2\alpha_j / k_{sj}. \quad (17)$$

The energy deposited in the bond as a result of bending can be obtained in a similar manner. Thus, the total energy deposited in the bond due to rotation is

$$E_{rj} = 2m_j^2 r_j^2 \omega^4 [(\sin^2\alpha_j / k_{bj}) + (\cos^2\alpha_j / k_{sj})]. \quad (18)$$

The energies deposited in other bonds can be calculated in a similar manner. The fraction of the rotational energy f_j deposited in bond j is

$$f_j = E_{rj}\left(\sum_{j=1}^{i-1} E_{rj}\right)^{-1}. \quad (19)$$

The rotational-energy change which is effective in the excitation of the bond j is

$$\Delta E_{rj} = f_j \Delta E_r = f_j \frac{1}{2}\sum m_i(\boldsymbol{\omega}\times\mathbf{r}_i)\cdot(\boldsymbol{\omega}\times\mathbf{r}_i)$$
$$+ f_i[V(\mathbf{b}_j) - V(\mathbf{a}_j)]. \quad (20)$$

Potential-Energy Change Due to Inelastic Stretching

The potential-energy change of the bond j due to the rotation of the molecule can be approximated by $[V(d_{ej}) - V(d_{0j})]$, where d_{0j} and d_{ej} are the jth bond distances before and after inelastic stretching. Using a quadratic potential function,

$$V(d_j) = V(d_{0j}) - \frac{1}{2}k_{sj}(d_j - d_{0j})^2 - V_{rj}, \quad (21)$$

where V_{rj} is the potential-energy change due to rotation of the molecule. As a result of conservation of angular momentum,

$$V_{rj} = \frac{1}{2}m_j(\omega a_j)^2(\cos^2\alpha_j)(a_j/r_j)^2. \quad (22)$$

For a small change, (r_j/a_j) may be approximated by (d_j/d_{0j}). Hence, from Eq. (21), the potential energy of the bond is

$$V(d_j) = V(d_{0j}) - \frac{1}{2}k_{sj}(d_j - d_{0j})^2$$
$$- \frac{1}{2}m_j(\omega a_j)^2(\cos^2\alpha_j)(d_{0j}/d_j)^2. \quad (23)$$

The new equilibrium distance d_{ej} is determined by $[\partial V(d_j)/\partial d_j]_{d_j=d_{ej}} = 0$, which results in

$$k_{sj}(d_{ej} - d_{0j}) - m_j(\omega a_j)^2(\cos^2\alpha_j)(d_{0j}^2/d_{ej}^3) = 0. \quad (24)$$

Combining Eqs. (20), (23), and (24),

$$\Delta E_{rj} = \frac{1}{2}f_j\sum m_i(\boldsymbol{\omega}\times\mathbf{r}_i)\cdot(\boldsymbol{\omega}\times\mathbf{r}_i)$$
$$- \frac{1}{2}k_{sj}d_{0j}^2[(d_{ej}/d_{0j}) - 1][(2d_{ej}/d_{0j}) - 1], \quad (25)$$

and the total energy increase in bond j is $\Delta E_j = \Delta E_{vj} + \Delta E_{rj}$, which is obtained from Eqs. (14) and (25).

Rotational and Vibrational Excitation in a Molecule

If a momentum impulse Q were acquired by an atom N in a time period so short that during that period it was not transmitted to the remainder of the molecule, then $\mathbf{S}_N = (\mathbf{Q}/m_N) + {}_0\mathbf{S}_N$, where ${}_0\mathbf{S}_N$ is the velocity of the atom N before acquiring the impulse and $\mathbf{S}_N$ the velocity following the impulse. Thus, ${}_0\mathbf{S}_i \approx \mathbf{S}_i$ for $i \neq N$. If the impulse $\mathbf{Q}$ is large compared to the momentum associated with the atoms of a thermal-energy molecule then, $\mathbf{S}_N = \mathbf{Q}/m_N$ and $\mathbf{S}_i \approx 0$ for $i \neq N$. From conservation of momentum and the definition of the space velocity,

$$\boldsymbol{\omega}\times\mathbf{r}_N + \mathbf{v}_N = \mathbf{Q}/m_N - \mathbf{Q}/\sum m_i$$
$$= [(\sum m_i - m_N)/(m_N \sum m_i)]\mathbf{Q}. \quad (26)$$

The first term on the left-hand side of Eq. (26) describes the rotational effect and $\mathbf{v}_N$ the vibrational effect of $\mathbf{Q}$ on the Nth atom.

We may resolve $\mathbf{Q}$ into a component $\mathbf{Q}_R$ which is perpendicular to $\mathbf{r}_N$ and results in a rotation of the
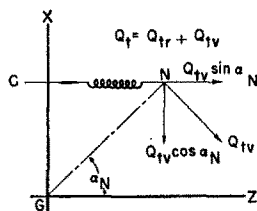
FIG. 2. Resolution of the momentum vector Q_t.

molecule and into a component $\mathbf{Q}_V$ which will be in a random direction and will result in a vibration in the molecule which is dependent on the strength of the bonds and the moments of inertia.

Equation (26) can be separated into

$$\omega \times \mathbf{r}_N = \left[\left(\sum m_i - m_N \right) / m_N \sum m_i \right] \mathbf{Q}_R \qquad (27)$$

and

$$\mathbf{v}_N = \left[\left(\sum m_i - m_N \right) / m_N \sum m_i \right] \mathbf{Q}_V. \qquad (28)$$

Realizing that there exists the relationships $\mathbf{r}_N \perp \omega$ and $\mathbf{r}_N \perp \mathbf{Q}_R$, it follows that

$$\omega = \left(\frac{\sum m_i - m_N}{m_N \sum m_i} \right) \left(\frac{\mathbf{Q}_R \times \mathbf{r}_N}{r_N^2} \right). \qquad (29)$$

For $k \neq N$,

$$\mathbf{v}_k = - \frac{\mathbf{Q}_V}{\sum m_i} - \frac{\mathbf{Q}_R}{\sum m_i} - \frac{\sum m_i - m_N}{m_N \sum m_i} \frac{(\mathbf{Q}_R \times \mathbf{r}_N) \times \mathbf{r}_k}{r_N^2}. \qquad (30)$$

Consequently, the vibrational-energy increase in bond N is

$$\Delta E_{vN} = \frac{1}{2} \frac{\sum m_i - m_N}{m_N \sum m_i} \left\{ Q_V^2 + (\mathbf{Q}_V \cdot \mathbf{Q}_R) \right.$$

$$\times \left[m_N r_N^2 - \left(\sum m_i - m_N \right) (\mathbf{r}_C \cdot \mathbf{r}_N) \right] / \sum m_i r_N^2$$

$$\left. + \frac{\sum m_i - m_N}{\sum m_i} \frac{(\mathbf{r}_C \cdot \mathbf{Q}_R)(\mathbf{r}_N \cdot \mathbf{Q}_V)}{r_N^2} \right\}. \qquad (31)$$

In order to resolve $\mathbf{Q}$ into $\mathbf{Q}_R$ and $\mathbf{Q}_V$ we define the molecular-coordinate system (x, y, z) choosing the center of mass G as the origin, and placing the bond N parallel to the z axis. The vector $\mathbf{Q}$ is resolved into Q_y, Q_t, and Q_r, where Q_y is parallel to y axis, Q_t is on the plane xz and is perpendicular to $\mathbf{r}_N$, and Q_r is in the direction of $\mathbf{r}_N$. Since Q_r passes through the center of mass G, it will not effect the rotation of the molecule. Q_y will cause both a bending vibration of bond N and a rotation of the molecule, particularly in x and z directions, i.e., ω_x and ω_z. Q_t will also cause both a bending and a stretching vibration of bond N as well as a rotation in y direction ω_y. Let us write

$$Q_y = Q_{yv} + Q_{yr}$$

and

$$Q_t = Q_{tv} + Q_{tr},$$

where Q_{yv} and Q_{tv} are momenta effective in the vibration of the bond N and Q_{yr} and Q_{tr} are momenta effec-

tive in the rotation of the molecule. We define the constants as given

$$F_{yv} = Q_{yv}^2 / Q_y^2, \qquad F_{yr} = Q_{yr}^2 / Q_y^2,$$

$$F_{tv} = Q_{tv}^2 / Q_t^2, \qquad F_{tr} = Q_{tr}^2 / Q_t^2.$$

Upon averaging we obtain

$$\langle Q_V^2 \rangle_{Av} = \frac{1}{3}(1 + F_{yv} + F_{tv}) Q^2 \qquad (32)$$

and

$$\langle \mathbf{Q}_V \cdot \mathbf{Q}_R \rangle_{Av} = \frac{1}{3}[(F_{yv} F_{yr})^{\frac{1}{2}} + (F_{tv} F_{tr})^{\frac{1}{2}}] Q^2 \qquad (33)$$

based on the fact that $\langle Q_r^2 \rangle_{Av} = \langle Q_y^2 \rangle_{Av} = \langle Q_t^2 \rangle_{Av} = \frac{1}{3} Q^2$. Defining as γ the angle between $\mathbf{r}_C$ and $\mathbf{r}_N$, the vibrational-energy increase in bond N is

$$\langle \Delta E_{vN} \rangle_{Av} = \frac{1}{6} \frac{Q^2}{m_N} \left(\frac{\sum m_i - m_N}{\sum m_i} \right) \left\{ 1 + F_{yv} + F_{tv} \right.$$

$$+ [(F_{yv} F_{yr})^{\frac{1}{2}} + (F_{tv} F_{tr})^{\frac{1}{2}}]$$

$$\left. \times \frac{[m_N - (\sum m_i - m_N)(r_C / r_N) \cos\gamma]}{\sum m_i} \right\}. \qquad (34)$$

It can be shown that when $r_N = a_N$,

$$\langle \omega_x^2 \rangle_{Av} = \left(\frac{\sum m_i - m_N}{\sum m_i} \right)^2 \left(\frac{Q^2}{3 m_N} \right) \frac{F_{yr} \cos^2\alpha_N}{m_N a_N^2}, \qquad (35)$$

$$\langle \omega_y^2 \rangle_{Av} = \left(\frac{\sum m_i - m_N}{\sum m_i} \right)^2 \left(\frac{Q^2}{3 m_N} \right) \frac{F_{tr}}{m_N a_N^2}, \qquad (36)$$

$$\langle \omega_z^2 \rangle_{Av} = \left(\frac{\sum m_i - m_N}{\sum m_i} \right)^2 \left(\frac{Q^2}{3 m_N} \right) \frac{F_{yr} \sin^2\alpha_N}{m_N a_N^2}, \qquad (37)$$

and

$$\langle \omega_x \omega_y \rangle_{Av} = \langle \omega_y \omega_z \rangle_{Av} = \langle \omega_z \omega_x \rangle_{Av} = 0. \qquad (38)$$

Also,

$$\langle \omega^2 \rangle_{Av} = \frac{Q^2}{3 m_N} \left(\frac{\sum m_i - m_N}{\sum m_i} \right)^2 \frac{F_{yr} + F_{tr}}{m_N a_N^2}. \qquad (39)$$

The total energy change in bond N will therefore be

$$\langle \Delta E_{iN} \rangle_{Av} = \frac{Q^2}{6 m_N} \left(\frac{\sum m_i - m_N}{\sum m_i} \right)^2 \left\{ \frac{\sum m_i}{\sum m_i - m_N} \left[1 + F_{yv} + F_{tv} \right. \right.$$

$$+ [(F_{yv} F_{yr})^{\frac{1}{2}} + (F_{tv} F_{tr})^{\frac{1}{2}}]$$

$$\left. \times \frac{m_N - (\sum m_i - m_N)(a_C / a_N) \cos\gamma}{\sum m_i} \right]$$

$$+ f_N \frac{F_{yr}(I_{xx} \cos^2\alpha_N + I_{zz} \sin^2\alpha_N) + F_{tr} I_{yy}}{m_N a_N^2}$$

$$\left. - (F_{yr} + F_{tr}) \cos^2\alpha_N (d_{0N}/d_{eN})^2 [2 - (d_{0N}/d_{eN})] \right\}. \qquad (40)$$

Estimation of Constants

Consider Q_t acting on the atom N as depicted in Fig. 2. As a result of Q_{tr}, the molecule will rotate and

the inertia opposing rotation will be I_{yy}. As a result of Q_{tv} the molecule will vibrate. The bond N will stretch and bend as a result of $Q_{tv} \sin\alpha_N$ and $Q_{tv} \cos\alpha_N$, respectively. If δ_{sN} is the maximum elongation of bond N due to $Q_{tv} \sin\alpha_N$, by energy balance we have

$$Q_{tv}^2 \sin^2\alpha/m_N = k_{sN}\delta_{sN}^2.$$

Similarly,

$$Q_{tv}^2 \cos^2\alpha/m_N = k_{bN}\delta_{bN}^2.$$

The degree of difficulty in deforming a bond increases as m_N, δ_{sN}, and δ_{bN} increase. Let us assume that the deformation inertia opposing Q_{tv} is

$$m_N(\delta_{bN}^2 + \delta_{sN}^2) = Q_{tv}^2\left(\frac{\cos^2\alpha_N}{k_{bN}} + \frac{\sin^2\alpha_N}{k_{sN}}\right) = \frac{Q_{tv}^2}{k_{tN}},$$

where

$$\frac{1}{k_{tN}} = \frac{\cos^2\alpha_N}{k_{bN}} + \frac{\sin^2\alpha_N}{k_{sN}}. \quad (41)$$

The total inertia opposing Q_t is therefore

$$[I_{yy} + (Q_{tv}^2/k_{tN})].$$

The fraction of inertia that is opposing Q_{tr} should also be the fraction of Q_t that is associated with Q_{tv}. Thus,

$$\frac{I_{yy}}{I_{yy} + (Q_{tv}^2/k_{tN})} = \frac{Q_{tv}}{Q_t}. \quad (42)$$

Solving Eq. (42) for Q_{tv}, it is found that

$$F_{tv}^{\frac{1}{2}} = Q_{tv}/Q_t = \frac{3}{2}(u_t)^{\frac{1}{2}}\{[1 + (1+u_t)^{\frac{1}{2}}]^{\frac{1}{3}} + [1 - (1+u_t)^{\frac{1}{2}}]^{\frac{1}{3}}\}, \quad (43)$$

where $u_t = 4k_{tN}I_{yy}/9Q^2$. In a similar manner,

$$F_{yv}^{\frac{1}{2}} = Q_{yv}/Q_y = \frac{3}{2}(u_y)^{\frac{1}{2}}\{[1 + (1+u_y)^{\frac{1}{2}}]^{\frac{1}{3}} + [1 - (1+u_y)^{\frac{1}{2}}]^{\frac{1}{3}}\}, \quad (44)$$

where

$$u_y = [4k_{bN}(I_{xx}\cos^2\alpha_N + I_{zz}\sin^2\alpha_N)]/9Q^2.$$

FAILURE TO BOND RUPTURE

When $\langle\Delta E_{iN}\rangle_{Av}$ attains the value of the dissociation energy of bond N E_{BN}, bond rupture results. Rearranging Eq. (40), the momentum required for bond rupture will be

$$Q^0 = \left\{\frac{6m_N E_{BN}}{(F_{yr} + F_{tr})\cos^2\alpha_N[B - d_N^{*2}(2 - d_N^*)]}\right\}^{\frac{1}{2}} \times \frac{\sum m_i}{\sum m_i - m_N}, \quad (45)$$

where

$$d_N^* = d_{0N}/d_{eN} \quad (46)$$

and

$$B = \frac{1}{(F_{yr} + F_{tr})\cos^2\alpha_N}\left[\frac{\sum m_i}{\sum m_i - m_N}\left(1 + F_{yv} + F_{tv} + [(F_{yv}F_{yr})^{\frac{1}{2}} + (F_{tv}F_{tr})^{\frac{1}{2}}]\right.\right.$$

$$\left.\times \frac{m_N - (\sum m_i - m_N)(a_C/a_N)\cos\gamma}{\sum m_i}\right)$$

$$\left. + f_N\frac{F_{yr}(I_{xx}\cos^2\alpha_N + I_{zz}\sin^2\alpha_N) + F_{tr}I_{yy}}{m_N a_N^2}\right]. \quad (47)$$

From Eqs. (24) and (45), B can also be evaluated in terms of the expression

$$B = \frac{2E_{BN}(d_N^*)^4}{k_{sN}d_{0N}^2(1 - d_N^*)} + d_N^{*2}(2 - d_N^*). \quad (48)$$

In the particular case where the atom receives a gamma-ray momentum impulse, the energy of the gamma ray required for bond rupture is $E_\gamma^0 = Q^0 c$, where c is the velocity of light.

CALCULATION OF Q°

To calculate the recoil momentum required for bond rupture, we used a method of successive approximations. The steps were: (1) calculating I_{xx}, I_{yy}, I_{zz}, $\cos\alpha_N$, and $\cos\gamma$ for each molecule using bond-distance and bond-angle data; (2) assuming a value of Q^0; (3) calcu-
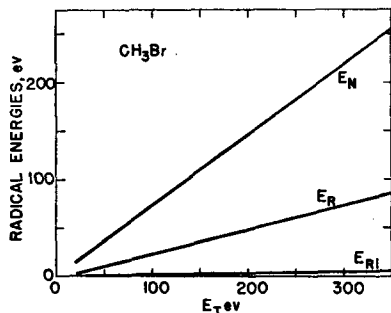
TABLE I. Minimum energy required and energy distribution for carbon-halogen bond rupture.[a]

Compound[b]	E_T^0 (ev)	E_N^0 / E_T^0 %	E_R^0 / E_T^0 %	E_{Ri}^0 / E_T^0 %	E_v^0 / E_T^0 %	E_r^0 / E_T^0 %
CH_3I	27.29	80.12	9.39	1.91	6.63	1.94
CD_3I	23.86	76.87	10.81	2.52	8.00	1.80
CF_3I	8.34	42.22	22.76	9.84	23.61	1.57
CH_2I_2	5.52	22.48	24.92	15.79	36.79	0.02
C_2H_5I	20.41	66.47	15.06	7.40	9.47	1.60
$i\text{-}C_3H_7I$	12.97	56.03	18.83	8.41	13.92	2.81
$n\text{-}C_3H_7I$	12.76	56.03	18.83	9.47	13.39	2.28
CH_3Br	20.74	70.91	13.30	1.66	11.12	3.01
CD_3Br	18.54	66.64	15.00	2.56	13.19	2.61
CF_3Br	7.38	28.83	24.86	8.38	37.29	0.64
CCl_3Br	4.06	16.25	24.06	7.49	52.18	0.02
CH_2Br_2	6.14	21.14	24.84	12.17	41.83	0.02
CF_2Br_2	4.90[c]	14.52	23.58	8.82	53.06	0.02
CCl_2Br_2	3.64[c]	10.84	22.09	8.84	58.23	0.00
$CHClBr_2$	4.93[c]	14.72	23.65	9.91	51.70	0.02
$CHBr_3$	4.76	9.99	21.63	12.29	56.09	0.00
CBr_4	2.98	5.82	18.28	4.86	71.04	0.00
C_2H_5Br	15.14	53.87	19.52	7.98	16.00	2.63
$1,1\text{-}C_2H_4Br_2$	5.78[c]	18.10	24.44	10.75	46.69	0.02
CH_3Cl	14.68	51.40	20.29	4.53	20.72	3.06
CD_3Cl	13.26	46.05	21.81	5.83	23.93	2.38
CF_3Cl	6.14	12.61	22.90	8.27	56.05	0.17
CHF_2Cl	7.13[c]	18.23	24.47	11.28	45.76	0.26
CH_2Cl_2	7.45	18.86	24.56	13.76	42.80	0.00
CF_2Cl_2	5.63	9.47	21.30	9.57	59.66	0.00
$CHCl_3$	5.16	9.71	21.44	12.81	56.04	0.00
$CFCl_3$	5.21	7.36	19.78	9.87	62.99	0.00
CCl_4	4.46	5.89	18.39	9.61	66.11	0.00

[a] The bond-dissociation energy, $E_{BN} = E_r^\circ + E_v^\circ$.

[b] The dissociating halogen is the last element listed in the formula.

[c] Based on estimated E_{BN}.

FIG. 3. Energy of radicals as a function of the total energy imparted to the Br atom in CH_3Br.

lating u_y, u_t, and consequently, F_{yr}, F_{yv}, F_{tr}, F_{tv}, and B using the assumed value of Q^0 and Eqs. (43), (44), and (47); (4) solving for $d_N{}^*$ in Eq. (48), using the value of B obtained in step 3, (5) calculating Q^0 by substituting the calculated values of F_{yr}, F_{tr}, B, and $d_N{}^*$ into Eq. (45) and then comparing with the assumed value of Q^0.

The minimum net recoil energies, $E_T{}^0 = (Q^0)^2/2m_N$, required for bond rupture were calculated for a series of halomethanes and are listed in Table I. It is noted that, in general, the heavier the mass of the radical attached to the activated atom, the smaller the net recoil energy required for bond rupture.

Also presented in Table I, as a percent of $E_T{}^0$, are the rotational- and vibrational-excitation energies received by the bond $(E_{BN} = E_v{}^0 + E_r{}^0)$, the recoil kinetic energies of the activated atom and the radical to which it was bonded, and the internal energy of the radical. For a diatomic molecule, Steinwedel and Jensen[3] have shown that $E_v/(E_v + E_r) = \frac{2}{3}$. Typical values of this quantity for the compounds in Table I are: CH_3Br—0.79, CD_3Br—0.84, CF_3Br—0.98, CCl_3Br—1.00, CBr_4—1.00. It is seen that the heavier the radical attached to the activated atom, the more unlikely is rotational excitation. This is to be expected since (1) an increase in molecular weight is accompanied by an increase in the moments of inertia, and (2) the bending-force constants for similar carbon-halogen bonds do not change appreciably. The net result is, that with increased molecular weight, rotation of the molecule becomes more difficult in comparison to the vibration of the molecule.

ENERGY OF RADICALS

Of the net recoil energy $E_T{}^0$ imparted to an atom, only a fraction of this energy is consumed in the bond rupture. Because the chemical reactivity of the radicals frequently depends upon their kinetic energy, it is of interest to determine the energies associated with the radicals.

If the net momentum Q exceeds that required for bond rupture Q^0 the total energy available to the newly formed radicals following bond rupture is the difference between the net-recoil energy acquired by the molecule $E_T = Q^2/2m_N$ and the bond dissociation energy E_{BN}. The total *kinetic energy* acquired by the two radicals is

equal to the kinetic energy of the parent molecule, $Q^2/2\sum m_i$, plus the bond-excitation energy which is in excess of the bond-dissociation energy, $\Delta E_{iN} - E_{BN}$.

The internal energy E_{Ri} associated with the radical, originally bonded to the activated atom, will therefore be equal to the total energy minus the bond-dissociation energy minus the kinetic energy of the radicals. Thus,

$$E_{Ri} = \frac{Q^2}{2m_N} - E_{BN} - \left[\frac{Q^2}{2\sum m_i} + \Delta E_{iN} - E_{BN} \right]$$

$$= \left[\frac{\sum m_i - m_N}{2m_N \sum m_i} - \frac{E_{BN}}{(Q^0)^2} \right] Q^2, \qquad (49)$$

where $\Delta E_{iN} = E_{BN} Q^2/(Q^0)^2$.

The velocity of the activated atom is $\mathbf{S}_N = \dot{\mathbf{R}} + \mathbf{v}_N$ and that of the radical is $\mathbf{S}_R = \dot{\mathbf{R}} + \mathbf{v}_R$. Because of conservation of momentum, $\mathbf{v}_N = -(\sum m_i - m_N)\mathbf{v}_R/m_N$. As a result of the conservation of energy, the energy associated with the activated atom is

$$\langle E_N \rangle_{Av} = \frac{m_N}{\sum m_i} \left\{ \frac{Q^2}{2\sum m_i} + \frac{\sum m_i - m_N}{m_N} \left[\frac{Q^2}{(Q^0)^2} - 1 \right] E_{BN} \right\}$$

$$(50)$$

and that of the radical originally bonded to the activated atom is

$$\langle E_R \rangle_{Av} = \frac{\sum m_i - m_N}{\sum m_i} \left\{ \frac{Q^2}{2\sum m_i} + \frac{m_N}{\sum m_i - m_N} \right.$$

$$\left. \times \left[\frac{Q^2}{(Q^0)^2} - 1 \right] E_{BN} \right\}. \quad (51)$$

The energy of the radicals as a function of the net recoil energy received by ^{80}Br in CH_3Br is presented in Fig. 3. It is noted that the energies of the radicals are approximately a linear function of the net recoil energy E_T. Thus, once the energy distribution between the radicals at the minimum recoil energy $E_T{}^0$ is known, the general trend of the energy distribution as a function of the net recoil energy E_T can be predicted. For a series of halomethanes, there are presented in Table I the energy distribution between the radicals evaluated at $E_T{}^0$; these values, therefore, represent the minimum kinetic energies $(E_N{}^0$ and $E_R{}^0)$ of the radicals.

BETA-RAY RECOIL

The emission of a beta particle in nuclear decay will result in a recoil momentum being imparted to the isotope. For example, the maximum ^{14}C beta-ray energy is 0.155 Mev; a beta ray of this energy will result in $E_T = (1.55 \times 10^5)/(14.01)(1836) = 6.02$ ev. The methods outlined above can be used to calculate the minimum recoil energy $E_T{}^0$ required for ^{14}N dissociation. If the beta spectrum is known, it is possible to determine the fraction of the nuclear disintegrations which will result in bond rupture.

Such calculations are being performed for $^{14}CO_2$, $^{14}C_2H_6$, and various tritiated compounds. The results will be reported in a separate communication.

SUMMARY

A molecule is visualized as being composed of a group of point-mass atoms joined together by springs. When one of the atoms in the molecule receives a momentum impulse Q the atom will dissociate from the molecule if $Q \geqq Q^0$. An equation is derived relating Q^0 to the bond energy, bond angles and distances, and the masses of the atoms in the molecule.

In deriving this expression, two major assumptions are made. They are:

(1) The rotational and vibrational motions of the molecule are independent and can therefore be separated.

(2) The momentum impulse is acquired by the atom in a time period which is short compared to the time required for dissociation of the atom. This dissociation time is probably of the order of 10^{-14} sec, the time required for one vibration. This is, perhaps, the most crucial assumption, leading to the approximation that atoms, other than the recoiling atom, do not experience an increase in space velocity. It is not obvious how to correct for this effect since the time sequence of momentum transfer through the molecule is not known. Since some intramolecular momentum transfer undoubtedly does occur, our calculated values of Q^0 must, of necessity, be low. The extent of correction needed to correct for this effect would probably depend upon the complexity of the molecule. Thus, for recoiling Br, Q^0 for CH_3Br could be closer to the correct value than would Q^0 for C_2H_5Br. Similarly, Q^0 for $i\text{-}C_3H_7I$ could be more correct than Q^0 for $n\text{-}C_3H_7I$ since, in the latter compound, the atoms, on the average, are separated from the recoiling iodine by a larger number of chemical bonds.