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Influence of Molecular Structure on Stopping Power of Chemical Species for He^+ Ions from a Low-Energy Particle Accelerator

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Since the early 1900s it has been known that the interposition of an absorbing medium in a beam of charged particles from a radioactive source or particle accelerator causes an energy loss of the particles. The energy loss is believed to be primarily through inelastic collisions between the moving ion and the bound electrons of the absorbing medium, since little or no scattering by the incident particle is observed.[1,2] The energy loss process is called the "stopping power" of the medium, a term which is logical when the incident particle is completely stopped, but which is still applied today, even when the particle is only slowed by the absorber. This stopping power is defined as[3]

$$\epsilon = \frac{\Delta E}{N\Delta x} \qquad (1)$$

where ΔE is the energy lost by the energetic ion in path length Δx when there are N atoms (or molecules) per unit volume of the stopping medium.

When ϵ is plotted as a function of the average energy of the moving ion in the stopping medium, a single peak is observed which falls off rapidly on the low-energy side and more slowly on the high-energy side. A typical stopping power distribution is shown in Figure 1 for cyclohexane vapor. Such a distribution can be characterized for the present discussion by three parameters: ϵ_{peak}, the maximum stopping power observed at the top of the peak; E_{peak}, the average He^+ ion energy at ϵ_{peak}; and δ, the peak width which is an indicator of the breadth of the stopping power distribution and here is arbitrarily defined as the length of a horizontal line in MeV which begins at ϵ(0.3 MeV) and terminates at the intersection of the line and the curve on the high-energy side of the peak.

This plot can be divided into three regions of ion energies representing three different relationships between stopping power and the number and type of electrons present in the absorber.

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(I) When the particle energy is sufficiently high that all electrons are stripped from the incident ion, the stopping power of the absorber is obtained theoretically[4,5] from the first Born approximation of quantum mechanics and is characterized by a single unknown parameter I, called the mean excitation potential.[2] This parameter includes excitation and ionization of both the inner shell and valence electrons of the stopping medium. This I value is usually given per atom of the stopping medium, but may be defined as a logarithmic average[6] over the I values of the constituent atoms of the molecule. At these high ion velocities, chemical binding effects are small (<1%) because the interaction with the tightly bound inner shell electrons contributes as much or more to energy loss as does interaction with the outer valence electrons. Small changes in I that correlate with bond order have been reported.[6-10]

(II) At ion velocities much less than those at the stopping power peak, the ion retains essentially its full complement of electrons and the energy loss will be mainly due[11] to the interaction of its own electronic structure with that of the target atoms.

(III) In the vicinity of the stopping power peak, not all inner shell electrons participate in the stopping process,[12] and higher order corrections to the Born approximation are needed.[13-18] The problem is further

(1) W. Whaling in "Nuclear Spectroscopy", Part A, F. Ajzenberg-Selove, Ed., Academic Press, New York, 1960, p 3.
(2) H. A. Bethe and J. A. Ashkin in "Experimental Nuclear Physics", Vol. I, E. Segrè, Ed., Wiley, New York, 1953, p 166.
(3) W. Whaling in "Handbuch der Physik", Vol. 34, S. Flügge, Ed., Springer-Verlag, Berlin, 1958, p 274.
(4) H. A. Bethe, *Ann. Phys.*, **5**, 325 (1930).
(5) F. Bloch, *Ann. Phys.*, **16**, 285 (1933); *Z. Phys.*, **81**, 383 (1933).
(6) U. Fano, *Annu. Rev. Nucl. Sci.*, **13**, 1 (1963).
(7) T. J. Thompson, *Univ. Calif. Radiat. Lab. Rept.*, No. 1910 (1952).
(8) W. Brandt, *Phys. Rev.*, **104**, 691 (1956); **105**, 1933 (1957).
(9) T. E. Burlin in "Radiation Dosimetry", Vol. I, F. H. Attix and W. C. Roesch, Eds., Academic Press, New York, 1968, p 331.
(10) G. D. Zeiss, W. J. Meath, J. C. F. MacDonald, and D. J. Dawson, *Radiat. Res.*, **70**, 284 (1977).
(11) J. A. Dennis and D. Powers, paper presented at the Sixth Symposium on Microdosimetry, Brussels, 1978.
(12) M. S. Livingston and H. A. Bethe, *Rev. Mod. Phys.*, **9**, 245 (1937); M. C. Walske, *Phys. Rev.*, **88**, 1283 (1952).
(13) J. C. Ashley, R. H. Ritchie, and W. Brandt, *Phys. Rev. B*, **5**, 2393 (1972).
(14) J. D. Jackson and R. L. McCarthy, *Phys. Rev. B*, **6**, 4131 (1972).
(15) K. W. Hill and E. Merzbacher, *Phys. Rev. A*, **9**, 156 (1974).

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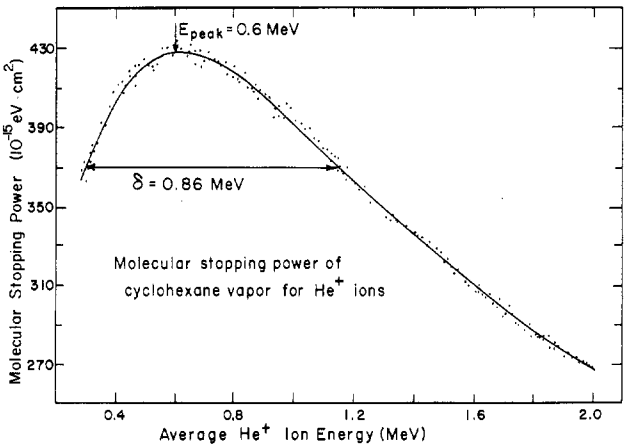

Figure 1. Molecular stopping power of cyclohexane vapor. The solid curve is a least-squares fit to the experimental data points. E_{peak} is the position of the maximum stopping power, and δ (see text) gives a measure of the width in MeV of the peak.

complicated because of capture and loss of electrons by the incident ion so that it is no longer fully ionized. The valence electrons of the absorbing medium become more involved in the stopping process at these lower ion velocities. Bohr[19] and Platzman[20] have indicated qualitatively that the maximum interaction between a colliding ion and target atom electron will occur when the velocities of the two are approximately the same, a condition which occurs for target atom valence electrons at ion velocities roughly in the vicinity of the stopping power peak. Thus, a study of bond order or chemical binding effects using stopping powers should be made with ions whose velocities are close to that of the stopping power peak where the relative contribution to stopping from inner shell electrons is less than that at higher ion velocities.

The approach used to determine the presence or absence of chemical-binding effects in the stopping power of a molecule is to apply the "Bragg rule",[21] first introduced in 1905, but which is still widely used today.[11,22] For a two-element compound A_iB_j the stopping power is simply the additive sum of the atomic stopping powers of the elements:

$$\epsilon(A_iB_j) = i\epsilon(A) + j\epsilon(B) \quad (2)$$

The stopping power ϵ per atom (or per molecule) is usually expressed in the units eV cm^2 and is a function of the velocity v_{ion} of the incident ion. A systematic study of this rule has been under way the past 10 years using He^+ ions where the stopping power of approximately 70 compounds in the vapor state has been measured[23-35] with relative probable error <1% and absolute error approximately 1–2% for He^+ ions of energy 0.3–2.0 MeV. The compounds include alkanes, alkenes, alkynes, *n*-alcohols, aldehydes, ketones, ethers, organic ring compounds, sulfur-containing organic and inorganic compounds, and halogen-containing compounds as well as simple gases such as hydrogen, oxygen, nitrogen, ammonia, carbon monoxide, and carbon dioxide. In the vicinity of the stopping power peak ($E_{He^+} \simeq 0.5$–0.9 MeV), deviations from Bragg's rule as great as 14.7% have been observed.[33]

When the stopping power peak parameters are examined in detail for a large number of compounds, the deviations from Bragg's rule can be related to the molecular structures of the compounds. A higher value of ϵ_{peak} is correlated to a higher bond order, and a higher peak energy E_{peak} is correlated to a lower bond order. The width δ of the peak is a strong function of the atomic constituents comprising the molecule.

Experimental Method

The apparatus for measuring stopping powers is shown in Figure 2. A He^+ ion beam from a Van de Graaff accelerator is focused and directed with initial energy E_i and typical beam current $\lesssim$200 nA through a differentially pumped gas cell system. The ion beam is positioned along the axis of the gas cell which is a stainless steel cylinder with open end windows pumped by a 6-in. diameter oil diffusion pump which constitutes the first differential pumping section. The entrance and exit ports connect to the second differential pumping sections which are pumped by 4-in. diameter oil diffusion pumps. The final ion beam energy, E_f, after passing through the gas cell system is measured by a 20° magnetic spectrometer. The beam current is detected at the Faraday cup by an electrometer, and is typically <10 nA or <1 pA if vapor is, respectively, absent or present in the gas cell.

A five-port manifold allows different gases or vapors to be remotely admitted in sequence to the gas cell. One of the ports is connected to nitrogen gas, whose molecular stopping power is measured each time that of a compound is measured so as to eliminate the possibility of any systematic deviations. If a liquid is used, it is contained in one of the stainless-steel supply cylinders. The vapor pressure in the gas cell is regulated from a few tenths to several torr and is measured by a capacitance manometer whose reading is totally independent of the composition or nature of the gas or vapor admitted to the gas cell. An electronic thermometer with transistor probe in close contact with the gas cell is used to measure the Kelvin temperature.

The molecular stopping power in 10^{-15} eV cm^2/molecule of a vapor or gas is given by eq 1, where $N = (9.656 \times 10^{15})P/T$, $\Delta E = E_i - E_f$ in keV, P is the pressure in torr, T is the temperature in Kelvins, and $\Delta x = 21.505$ cm is the length of the gas cell. N is the number of molecules per unit volume in the gas cell.

(16) J. Lindhard, *Nucl. Instr. Meth.*, **132**, 1 (1976).
(17) H. H. Andersen, J. F. Bak, H. Knudsen, and B. R. Nielsen, *Phys. Rev. A*, **16**, 1929 (1977).
(18) H. H. Andersen, J. F. Bak, H. Knudsen, P. Møller Peterson, and B. R. Nielsen, *Nucl. Instr. Meth.*, **140**, 537 (1977).
(19) N. Bohr, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **18**, No. 8 (1948).
(20) R. L. Platzman in "Symposium on Radiobiology", J. J. Nickson, Ed., Wiley, New York, 1952, p 139.
(21) W. H. Bragg and R. Kleeman, *Philos. Mag.*, **10**, S 318 (1905).
(22) W. Neuwirth, W. Pietsch, and R. Kreutz, *Nucl. Instr. Meth.*, **149**, 105 (1978).
(23) W. K. Chu and D. Powers, *Phys. Rev.*, **187**, 478 (1969).
(24) P. D. Bourland, W. K. Chu, and D. Powers, *Phys. Rev. B*, **3**, 3625 (1971).
(25) P. D. Bourland and D. Powers, *Phys. Rev. B*, **3**, 3635 (1971).
(26) W. K. Chu and D. Powers, *Phys. Rev. B*, **4**, 10 (1971).
(27) D. Powers, W. K. Chu, R. J. Robinson, and A. S. Lodhi, *Phys. Rev. A*, **6**, 1425 (1972).
(28) D. Powers, A. S. Lodhi, W. K. Lin, and H. L. Cox, Jr., *Thin Solid Films*, **19**, 205 (1973).
(29) A. S. Lodhi and D. Powers, *Phys. Rev. A*, **10**, 2131 (1974).
(30) E. K. L. Chau, R. B. Brown, A. S. Lodhi, D. Powers, S. Matteson, and S. R. Eisenbarth, *Phys. Rev. A*, **16**, 1407 (1977).
(31) E. K. L. Chau, D. Powers, A. S. Lodhi, and R. B. Brown, *J. Appl. Phys.*, **49**, 2346 (1978).
(32) E. K. L. Chau and D. Powers, *J. Appl. Phys.*, **49**, 2611 (1978).
(33) R. B. Brown and D. Powers, *J. Appl. Phys.*, **50**, 5099 (1979).
(34) D. Powers and H. G. Olson, *J. Chem. Phys.*, **73**, 2271 (1980).
(35) H. G. Olson and D. Powers, to be published in *J. Appl. Phys.*

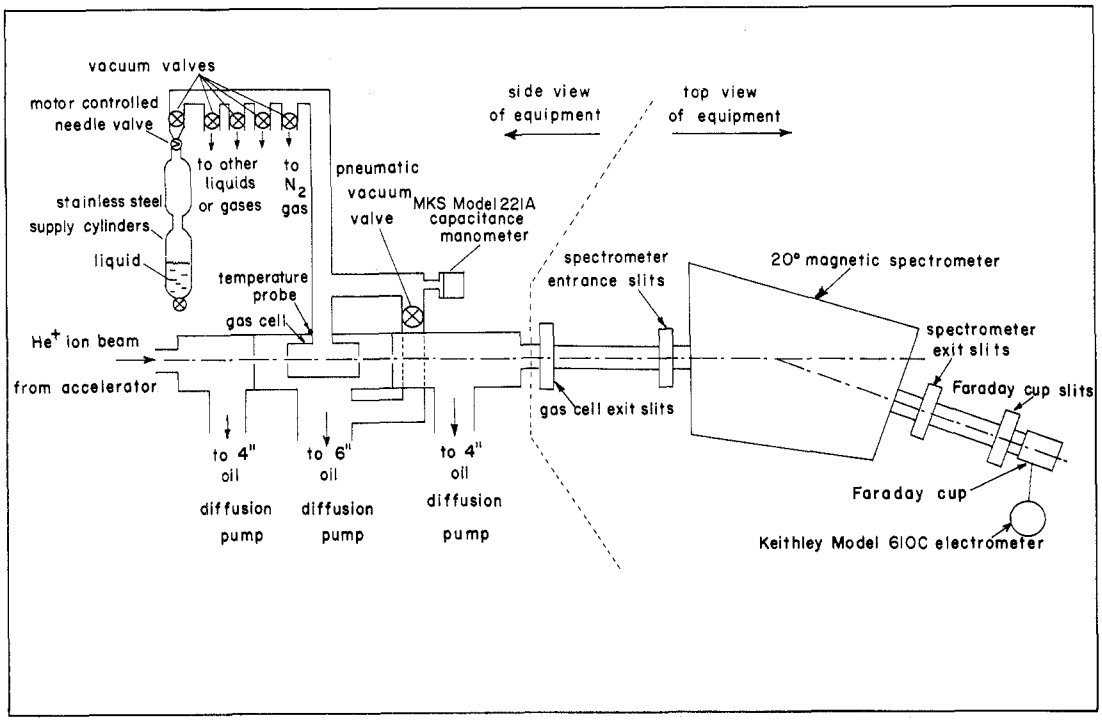

Figure 2. Experimental arrangement.

Corrections were made to the stopping powers for known impurities in the compounds by use of Bragg's rule and were no greater than 0.1%. The energy at which the stopping power was determined was the average energy $E_{av} = (E_i + E_f)/2$. Corrections to gas cell length and average energy along with those due to multiple scattering and localized heating effects are discussed along with details of the differential pumping system in ref 24. A discussion of random and systematic errors is provided in ref 30 and 33.

A typical energy spectrum from which molecular stopping powers are obtained is given in Figure 3 for cyclohexane vapor. The narrow peak of width $\delta_1 = 2.2$ MeV at $E_i = 900.0$ keV was obtained with no cyclohexane vapor in the gas cell. After cyclohexane vapor was admitted to the gas cell and stabilized to a pressure of 0.343 torr at $T = 300.2$ K, the energy distribution was broadened to $\delta_2 = 16.1$ keV and the center of the peak was lowered in energy to $E_f = 802.5$ keV. The mean energy loss of the He^+ ions in the gas cell of length $\Delta x = 21.505$ cm is $\Delta E = E_i - E_f = 97.5$ keV. These values, when substituted into eq 1, give a stopping power for cyclohexane vapor of 411×10^{-15} eV cm^2/molecule. The broadened width δ_2 is due to a combination of instrumental resolution, energy straggling, and energy dispersion in the 20° magnetic spectrometer.

The number of stopping power measurements ranges from about 150 to over 600 per compound and at average He^+ energies from 0.3 to 2.0 MeV. All stopping powers were checked and remeasured on at least two different occasions and often even more. A least-squares curve fit to the experimental points is made for the function

$$\epsilon(E) = a_0 + a_1E + a_2E^2 + a_3E^3 + a_4E^4 \qquad (3)$$

for the energy region $0.3 \leq E \leq E_B$ and

$$\epsilon(E) = (C/E) \ln (DE) \qquad (4)$$

for the energy interval $E_B < E \leq 2.0$ MeV. The parameters were chosen so that the logarithmic derivatives of the two fitting junctions joined smoothly at the boundary E_B which for cyclohexane was 1.4 MeV. The basis for the use of these functions is given in ref 27.

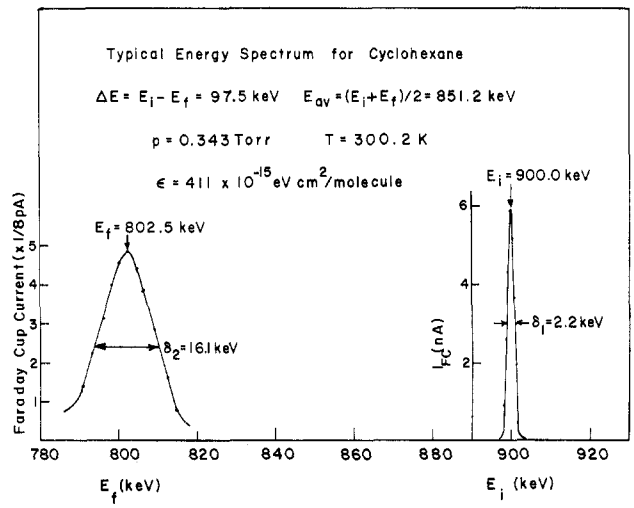

Figure 3. Typical energy spectrum for cyclohexane vapor from which stopping powers are determined.

Evidence for Chemical Binding Effects

The Bragg rule (eq 2) can be written for hydrocarbons in the form $\epsilon(H) = -(i/j)\epsilon(C) + (1/j)\epsilon_{expt}(C_iH_j)$ and then treated as a purely linear algebraic equation, $y = -ax + b$, which is a straight line whose slope is $-a = -i/j$, the negative ratio of the number of carbon to hydrogen atoms in the molecule. The ordinate intercept is $(1/j)\epsilon_{expt}(C_iH_j)$, where "expt" means the experimentally measured value. For each of the 20 hydrocarbons at a fixed He^+ ion energy, the value $(1/j)\epsilon_{expt}(C_iH_j)$ is first calculated and entered on the y axis as a point; a line of negative slope $-a = -i/j$ is then drawn through this point. A family of 20 straight lines is thereby obtained which essentially provides a graphical method for

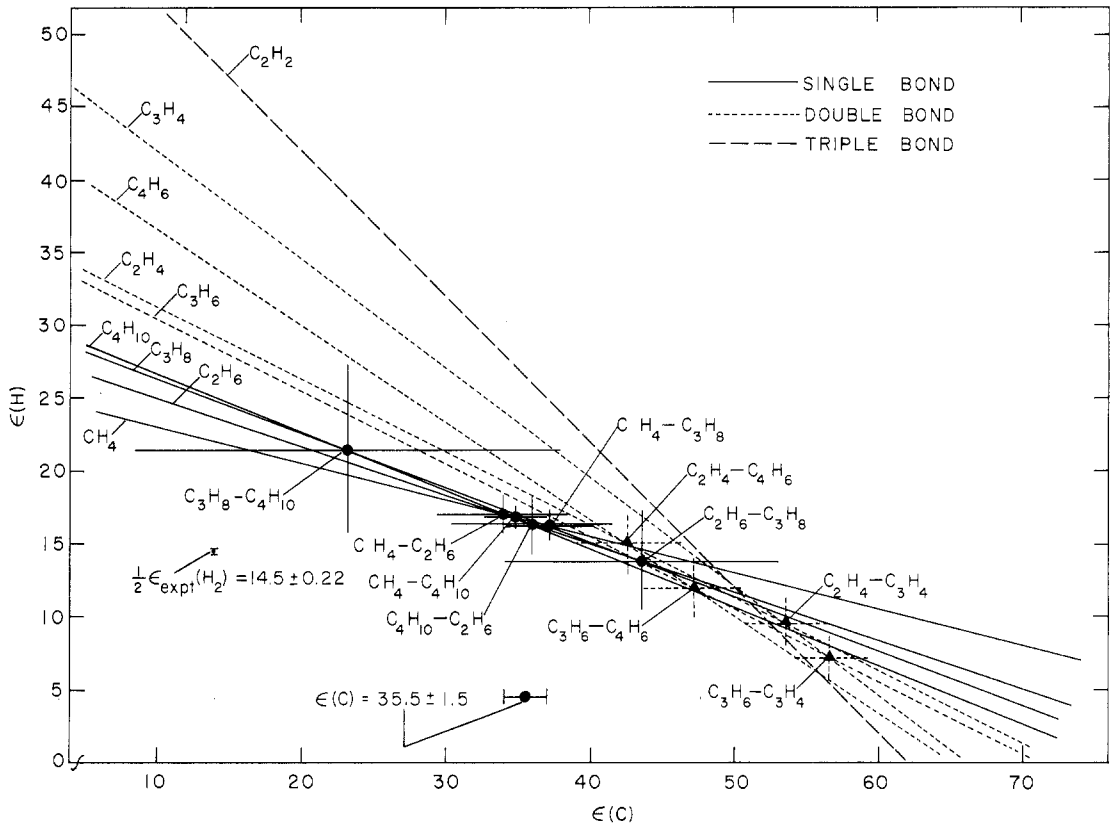

Figure 4. Linear plot of ϵ(H) vs. ϵ(C) at E_{av} = 0.5 MeV by use of Bragg rule to demonstrate effect of bond order for nine C–H compounds. The values of $\epsilon(C) = 35.5 \pm 1.5$ and $^1/_2\epsilon_{expt}(H_2) = 14.5 \pm 0.22$ ($\times 10^{-15}$ eV cm^2) are shown for comparison and are that of vapor-deposited solid carbon[23] and hydrogen gas.[24] The dots and triangles represent simply the intersection of lines whose compounds are single bonded and which contain double bonds, respectively. Also, the error bars are the square root of the geometric mean of probable errors of the ϵ measurements of the two compounds. For example, for the pair CH_4 and C_2H_6, $\epsilon(C) = 2\epsilon_{expt}(C_2H_6) - 3\epsilon_{expt}(CH_4) \pm [(2\Delta\epsilon_{C_2H_6})^2 + (3\Delta\epsilon_{CH_4})^2]^{1/2}$, where $\Delta\epsilon_{C_2H_6}$ and $\Delta\epsilon_{CH_4}$ are probable errors in the C_2H_6 and CH_4 measurements at E_{av} = 0.5 MeV. Reproduced with permission from ref 29. Copyright 1974, American Institute of Physics.

solving 20 simultaneous equations. If chemical binding plays no role in the stopping process, then Bragg's rule holds and all 20 lines will intersect at a common point $(x,y) = (\epsilon(C),\epsilon(H))$ except for those parallel lines which have the same i/j ratio.

An attempt to solve 9 of the 20 equations using the experimental stopping powers at E_{av} = 0.5 MeV for 9 of the 20 compounds is shown in Figure 4 and clearly reveals that no common values of ϵ(C) and ϵ(H) exist for these nine compounds of widely differing chemical structure. The plot instead reveals $\epsilon_{SB}(C) < \epsilon_{DB}(C) < \epsilon_{TB}(C)$, with ϵ(H) decreasing from single-bond to triple-bond compounds (SB, DB, TB = single, double, and triple bonds). Also, ϵ_{SB}(C) appears to have the same numerical value as vapor-deposited solid carbon, whereas ϵ_{SB}(H) is greater than the experimental $(1/2)\epsilon_{expt}(H_2)$. When similar lines are plotted for the cycloalkanes, the ring structure is clearly manifested, with a higher ϵ(C) being observed as the number of CH_2 groups decreases from cyclooctane to cyclopropane.

An alternate approach is given in Figure 5 at E_{av} = 0.6 MeV, where the experimental stopping powers for the normal alkanes, alcohols, ethers, and cycloalkanes are plotted in terms of integral multiples n of $\epsilon(CH_2)$. For the n-alkanes, Bragg's rule may be written as $\epsilon_{expt}(C_nH_{2n+2}) = n\epsilon(CH_2) + 2\epsilon(H)$. A plot of ϵ_{expt} vs. n for the compounds methane (n = 1) through butane (n = 4) reveals a linear dependence, with the slope of the line being $\epsilon(CH_2) = 70.9 \pm 1.4 \times 10^{-15}$ eV cm^2 and the ordinate intercept being $2\epsilon(H) = 32.2 \pm 2.4 \times 10^{-15}$ eV cm^2, which is 10.5% higher than $\epsilon_{expt}(H_2)$ and is similar to the higher ϵ_{SB}(H) obtained for alkanes as compared to $(1/2)\epsilon_{expt}(H_2)$ in Figure 4.

In the center portion of Figure 5 is plotted $\epsilon_{expt}(C_nH_{2n+1}OH) = n\epsilon(CH_2) + \epsilon(HOH)$ as a function of n for the normal alcohols methanol (n = 1) through propanol (n = 3). On the same plot is $\epsilon_{expt}((C_{n'}H_{2n'+1})_2O) = 2n'\epsilon(CH_2) + \epsilon(HOH)$ vs. n for the normal ethers dimethyl ether, $n' = n/2 = 1$, and diethyl ether, $n' = n/2 = 2$. The slope of the straight line through the experimental points is $\epsilon(CH_2) = 70.4 \pm 1.4 \times 10^{-15}$ eV cm^2, which compares extremely well to that of $70.9 \pm 1.4 \times 10^{-15}$ eV cm^2 from the normal alkanes. The ordinate intercept of the line is $\epsilon(HOH) = 73.6 \pm 2.4 \times 10^{-15}$ eV cm^2, which is in excellent agreement with $\epsilon_{expt}(H_2O$ vapor$) = 73.4 \pm 0.7 \times 10^{-15}$ eV cm^2. These considerations lend support in normal alkanes, alcohols, and ethers to the existence of a common ϵ_{SB}(H), ϵ_{SB}(C), and ϵ_{SB}(0) which are, respectively, 10% higher, equal to, and 17% lower than $^1/_2\epsilon_{expt}(H_2)$, vapor-deposited ϵ(C), and $^1/_2\epsilon_{expt}(O_2)$ at ion energies close to the stopping power curve peak.

Since the cycloalkane family all have molecular ring structures which are integral multiples of the group (CH_2), it is of interest to compare $\epsilon_{expt}((CH_2)_n)$ to integral multiples of $\epsilon(CH_2)$ obtained from normal alkanes. This comparison is given in the lower portion of Figure 5 for cycloethane = ethylene (n = 2) to cyclooctane (n = 8), with the difference between experiment and calculation being shown in parentheses. This

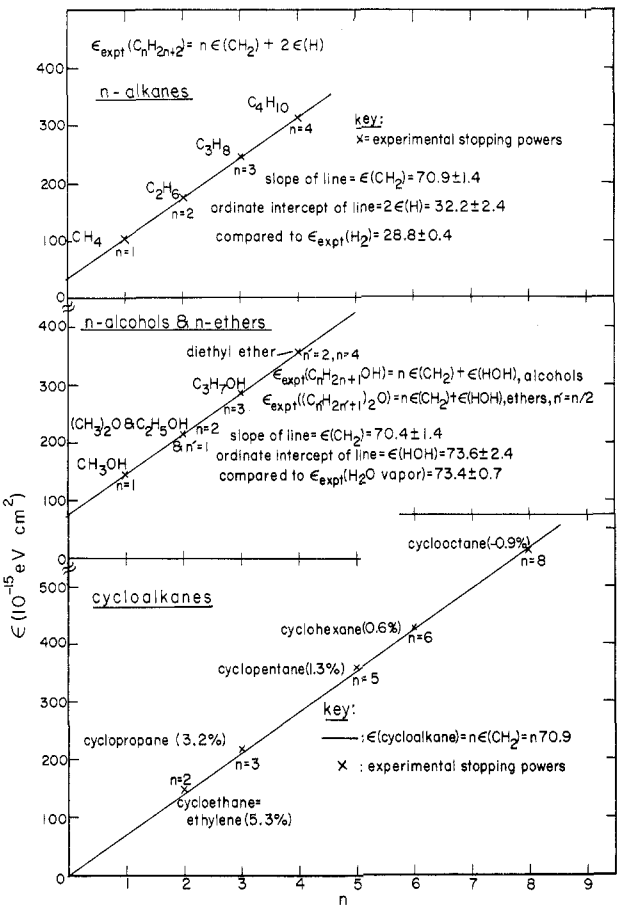

Figure 5. Molecular stopping powers of normal alkanes, alcohols, ethers, and cycloalkanes plotted as a function of the number n of (CH_2) groups in the compounds. The figure demonstrates a common $\epsilon(CH_2)$, $\epsilon(H)$, $\epsilon(C)$, and $\epsilon(O)$ for the normal alkanes, alcohols, and ethers but indicates a higher stopping power correlated to tighter ring structure in cycloalkanes when $n \leq 5$.

difference is even greater if $\epsilon(CH_2)$ from the normal alcohols and ethers is used. Since the relative error in the experiment is <1%, a clear ring-structure effect is seen when there are $n \leq 5$ (CH_2) groups in the ring. The "tighter" ring structure is accompanied by a higher stopping power value.

The replacement of a (CH_2) group by O in ring structures to obtain ethylene oxide, propylene oxide, and *p*-dioxane reveals[31-33] $\epsilon_{RING}(O) > \epsilon_{SB}(0)$, while for cyclohexanone an $\epsilon_{DB}(O) \simeq {}^1/_2\epsilon_{expt}(O_2)$ is obtained. A study of the stopping powers of cycloalkanes along with the effect of radicals external to a benzene ring also correlates to a higher stopping power of $\epsilon(C)$ associated with the double bond, and an even higher one for the triple-bonded carbon in phenylacetylene. Evidence for resonance effects as well as correlations to bond-strain energy is also seen.[33]

From stopping power measurements of vapors from five aldehydes and ketones the effect of the C–O double bond has also been studied,[32] which when coupled with the ring compounds and ethers, establishes a hierarchy $\epsilon_{DB}(O) > \epsilon_{RING}(O) > \epsilon_{SB}(0)$, with the maximum difference being about 17%. The stopping power peak occurs at $E_{peak} = 0.75$ MeV for $\epsilon_{DB}(O)$ and at $E_{peak} \simeq 1.0$ MeV for $\epsilon_{SB}(0)$. Similar behavior is observed for the atomic stopping powers of solid carbon[36] where ϵ(graphite) (a network of benzene-like rings[37]) > vapor-deposited $\epsilon(C)$ by as much as 28%. The peak position is $E_{peak} = 0.52$ MeV for graphite and 0.75 MeV for vapor-deposited carbon, whose structure has been reported to be that of microscopic regions of ordered, covalently bonded carbon.[38] Thus, the higher bond order correlates to a higher stopping power value but to a lower peak position energy E_{peak}. The same behavior $\epsilon_{DB}(S) > \epsilon_{RING}(S) > \epsilon_{SB}(S)$ has also been observed[34,35] in sulfur-containing compounds, although to a lesser degree, viz., the maximum difference between $\epsilon_{DB}(S)$ and $\epsilon_{SB}(S)$ is only about 5%.

Bond Order in C–H–O Isomers

In Figure 6 is plotted peak (maximum) stopping power as a function of the peak energy E_{peak} in MeV. Although the ordinate scale is greatly reduced and the effect may not be explicit in the figure, an interesting comparison may nevertheless be made among some C–H–O isomers which confirms the trends reported in the previous section. For the sake of simplicity, the units of 10^{-15} eV cm^2 will be dropped in the discussion. First, the two C_2H_6O isomers ethanol and dimethyl ether have almost identical stopping powers, 214.5 ± 1.5 and 214.9 ± 1.1, respectively, as expected, since they are both single bonded. The two C_4H_8O isomers, 2-butanone and butyraldehyde, both having C–O double bonds, also have identical stopping powers, 335.4 ± 2.3 and 332.9 ± 2.3, respectively, within experimental error. On the other hand, the C_2H_4O isomers acetaldehyde (one C–O double bond) and ethylene oxide (three-membered-ring structure) have values 193.2 ± 1.4 and 189.5 ± 1.1, respectively, which are far enough outside experimental error to indicate a real bond-order effect. A "single bond value" for C_2H_4O calculated from ϵ(ethanol) − $2\epsilon_{SB}(H)$ would be expected to be 182.7 ± 2.8, which is lower and outside experimental error from either the aldehyde or the ring. A fourth comparison may be made among the C_3H_6O isomers. The stopping powers of vinyl methyl ether (one C–C double bond), acetone (one C–O double bond), propylene oxide (three-membered ring), and ϵ(propanol) − $2\epsilon_{SB}(H)$ (single-bonded) are, respectively, 266.0 ± 2.1, 262.9 ± 1.8, 258.8 ± 2.3, and 252.8 ± 2.9. The compounds vinyl methyl ether and acetone, both with double bonds, agree to within experimental error, but are consistently higher than their ring-structure and "single bond values". Thus, the hierarchy $\epsilon_{DB} > \epsilon_{RING} > \epsilon_{SB}$ is seen directly from the actual experimental molecular stopping powers as well as from atomic stopping powers calculated from them.

Peak Stopping Power and Position

In Figures 6 and 7 are plotted, respectively, the peak stopping power in 10^{-15} eV cm^2 and peak width δ(MeV) as a function of E_{peak}. It is immediately apparent from these figures that peak energies E_{peak} and peak width δ are lowest for compounds containing sulfur, higher for hydrocarbons, higher still for C–H–O compounds, and highest for fluorine-containing compounds. A summary

(36) S. Matteson, E. K. L. Chau, and D. Powers, *Phys. Rev. A*, 14, 169 (1976).

(37) B. H. Mahan, "University Chemistry", Addison-Wesley, Reading, MA, 1965, p 492.

(38) R. D. Heidenreich, *J. Electromicrosc. (Tokyo)*, 16, 23 (1967).

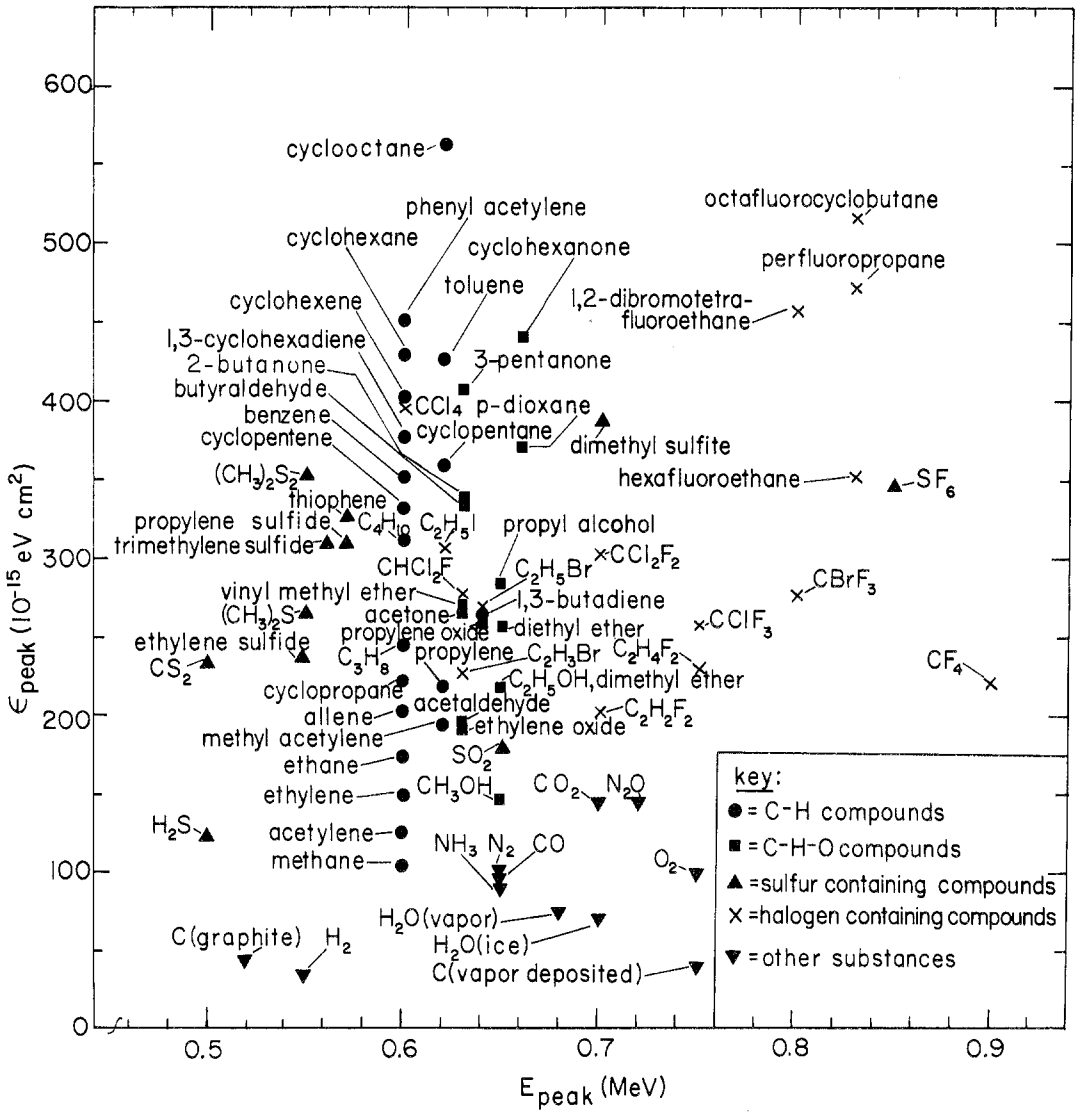

Figure 6. Molecular stopping power ϵ_{peak} as a function of the energy E_{peak} at which the maximum stopping power is observed.

of these two figures is provided below.

C–H Compounds

Of 20 C–H compounds, 15 have their peak position at 0.6 MeV, 4 (cyclopentane, toluene, propylene, and methylacetylene) at 0.62 MeV, and one at 0.64 MeV (1,3-butadiene). The average value of the peak position is 0.606 MeV. The peak width δ varies from 0.72 MeV (C_2H_2) to 0.91 MeV (propylene) and has an average value of 0.828 MeV. Although four of the five compounds with higher peak energies have a partial double-bond or triple-bond character, so also do seven of the compounds which peak at 0.6 MeV. Thus, no conclusion is explicit with regard to dependence of bond order on E_{peak} or δ for C–H compounds.

C–H–O Compounds

Of 16 C–H–O compounds, E_{peak} varies from 0.63 to 0.66 MeV (average value of 0.642 MeV, which is 0.036 MeV higher than that of C–H compounds). The peak width δ varies from 0.85 to 0.95 MeV and has an average value for the 16 compounds of 0.91 MeV. The compounds ethylene oxide and propylene oxide and those with double bonds (aldehydes and ketones) peak at lower energies (0.63 and 0.64 MeV), whereas the normal alcohols and ethers (of lower bond order) peak at the higher energy 0.65 MeV. Thus, the presence of oxygen results in a broader distribution which peaks at higher energy and whose peak position correlates well to bond order: the higher peak energy corresponds to a lower bond order.

Sulfur-Containing Compounds

For eight compounds containing C, H, and S, the peak position varies from 0.5 to 0.57 MeV and peak width δ from 0.575 to 0.77 MeV. The presence of sulfur clearly shifts both peak position and width to lower energies. As in the case of the C–H compounds, not much can be said about bond order for these compounds since CS_2 and H_2S (having quite different bond order) have essentially the same peak energies and widths. On the other hand, when oxygen is present, as for example in SO_2 and dimethyl sulfite, the peak position is shifted higher to 0.65 and 0.70 MeV, respectively, and both widths are considerably broadened.

Methane-Type Compounds

The seven methane-type compounds are listed in Table I as a function of peak energy and peak width δ. These compounds are all single bonded. The effect of F is clearly seen: as the number of F atoms increases, so does the peak width and peak energy. The effect of

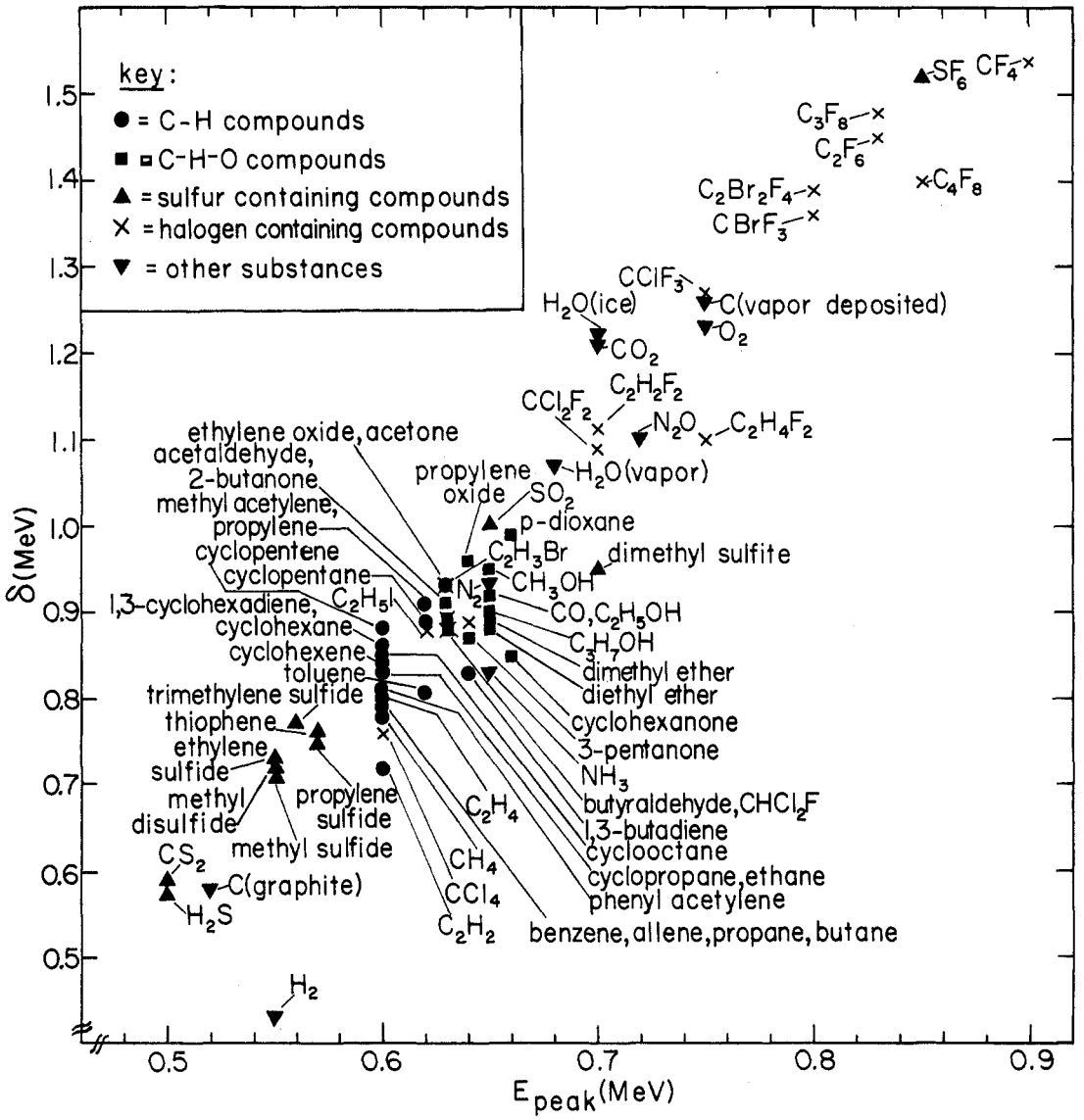

Figure 7. Width, δ, in MeV of the stopping power curve as a function of E_{peak}.

Table I
Stopping Power Peak Energy and Width for Methane-Type Compounds[a]

compd	peak energy, MeV	peak width, MeV	bond	bond energy, kcal/mol	bond length, Å	electronegativity difference
CF_4	0.90	1.54	C-F	105.4	1.37	1.5
$CBrF_3$	0.80	1.36	C-H	98.8	1.095	0.4
$CClF_3$	0.75	1.27	C-Cl	78.5	1.76	0.5
CCl_2F_2	0.70	1.09	C-Br	65.9	1.94	0.3
$CHCl_2F$	0.63	0.88				
CH_4	0.60	0.78				
CCl_4	0.60	0.76				

[a] Included also are bond energies, bond lengths, and electronegativity differences from Pauling.[39]

the C–H and C–Cl bond on peak position and width is seen to be approximately the same since CH_4 and CCl_4 have roughly the same peak position and width. When one of the F atoms in CCl_2F_2 is replaced by a H atom, the peak energy and width (in $CHCl_2F$) are lowered by 0.07 and 0.21 MeV, respectively, whereas when one of the F atoms in CF_4 is replaced by either Br or Cl, the effect is about the same. This implies that the C–H, C–Br, and C–Cl contribution to peak location and width is about the same, but that the C–F contribution is greater. No correlation between bond energy or bond length with stopping power peaks or widths is seen from the table. The fact that the amount of ionic character in the bond is greater by a factor of 3 to 5 for the C–F bond than the other may, however, be indicative of a correlation of electronegativity with the experimental observations.

Concluding Remarks

The only theoretical concept mentioned here to interpret the stopping powers has been that of bond order. Other theoretical concepts such as strain energy[33] and density of final states[36] have also been used to interpret the stopping power data, and further work

with these and other concepts is clearly needed. Nevertheless, it has been demonstrated in measured or calculated atomic stopping powers that the hierarchy double bond > ring structure > single bond holds for C, O, and S with maximum differences $\simeq$ 28%, 17%, and 5%, respectively. It is proposed that stopping power measurements may serve as a useful supplement to existing spectroscopic techniques currently used by chemists to determine bond order. For example, stopping powers can be used[34] to assign a resonance hybrid structure[39] consisting of one S–O double bond and one S–O single bond for SO_2 and a single coordinate covalent bond for the third oxygen atom in dimethyl sulfite, in contradistinction to double-bonded structures predicted by Gillespie's VSEPR model[40] which requires d-orbital participation.

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Supplementary Material Available: Table of three stopping power parameters E_{peak}, ϵ_{peak}, and δ used to characterize the stopping power curve for 72 substances (2 pages). Photocopies of this material or microfiche (105 × 148 mm, 24× reduction negatives) may be obtained from Business Operations, Books and Journal Division, American Chemical Society, 1155 16th St., NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, author) and prepayment (check or money order) for $5.50 for photocopy or $3.00 for microfiche (include $1.00 additional postage for foreign mail) are required.

(39) L. Pauling, "The Chemical Bond", Cornell University Press, Ithaca, N.Y., 1967.

(40) R. J. Gillespie, *J. Chem. Educ.*, **40**, 479 (1961).

Variational Transition-State Theory

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The two most accurate practical methods for calculating the rate constants for thermally activated bimolecular reactions in the gas phase are trajectory calculations[1-3] and transition-state theory. In conventional formulations the transition state is a surface in configuration space that divides reactants from products and passes through the saddle point of the potential-energy surface.[4-10] In order to improve on this treatment, we have been studying the effects on the computed rate constants of using generalized transition states. Generalized transition states are surfaces in phase space dividing reactants from products but not necessarily passing through a saddle point. Instead we determine the position of the dividing surface using a variational criterion.[11-17] This general procedure is called variational transition-state theory. We have recently completed several applications[17-24] and a preliminary review[2] for collinear reactions and several applications[21,22,25-30] to three-dimensional reactions. In this Account we provide a general introduction to this work and survey some of the results.

It is customary to derive transition-state theory by postulating a quasiequilibrium between transition-state species and reactants.[4-10] Although this is valid, the conditions for validity of transition-state theory become

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(1) R. N. Porter, *Annu. Rev. Phys. Chem.*, **25**, 317 (1974).
(2) D. G. Truhlar, *J. Phys. Chem.*, **83**, 188 (1979).
(3) D. G. Truhlar and J. T. Muckerman in "Atom-Molecule Collision Theory: A Guide for the Experimentalist", R. B. Bernstein, Ed., Plenum Press, New York, 1979, p 505.
(4) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes", McGraw-Hill, New York, 1941.
(5) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, 1966.
(6) D. L. Bunker, "Theory of Gas Phase Reaction Rates", Pergamon press, Oxford, 1966.
(7) K. J. Laidler, "Theories of Chemical Reaction Rates", McGraw-Hill, New York, 1969.
(8) R. E. Weston, Jr. and H. A. Schwartz, "Chemical Kinetics", Prentice-Hall, New York, 1972.
(9) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.
(10) R. P. Wayne in "Comprehensive Chemical Kinetics", Vol. 2, C. M. Bamford and C. F. H. Tipper, Eds., Elsevier, Amsterdam, 1969, p 189.
(11) E. Wigner, *J. Chem. Phys.*, **5**, 720 (1937).
(12) J. Horiuti, *Bull. Chem. Soc. Jpn.*, **13**, 210 (1938).
(13) J. C. Keck, *J. Chem. Phys.* **32**, 1035 (1960).
(14) J. C. Keck, *Adv. Chem. Phys.*, **13**, 85 (1967).
(15) P. Pechukas in "Dynamics of Molecular Collisions, Part B", W. H. Miller, Ed., Plenum Press, New York, 1976, p 269.
(16) B. C. Garrett and D. G. Truhlar, *J. Chem. Phys.*, **70**, 1593 (1979).
(17) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **83**, 1052, 3058E (1979).
(18) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **84**, 805 (1980).
(19) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **83**, 200, 3058E (1979).
(20) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **83**, 1079 (1979); **84**, 682E (1980).
(21) B. C. Garrett, D. G. Truhlar, R. S. Grev, and A. Magnuson, *J. Phys. Chem.*, **84**, 1730 (1980).
(22) B. C. Garrett, D. G. Truhlar, and R. S. Grev, *J. Phys. Chem.* **84**, 1749 (1980).
(23) B. C. Garrett, D. G. Truhlar, R. Grev, A. Magnuson, and J. N. L. Connor, *J. Chem. Phys.*, **73**, 1721 (1980).
(24) B. C. Garrett, D. G. Truhlar, R. Grev, and R. B. Walker, *J. Chem. Phys.*, **73**, 235 (1980).
(25) B. C. Garrett and D. G. Truhlar, *J. Am. Chem. Soc.*, **101**, 4534 (1979).

0001-4842/80/0113-0440$01.00/0