PHYSICAL REVIEW A VOLUME 22, NUMBER 6 DECEMBER 1980

Analysis of electronic stopping cross sections of organic molecules

Ronald Kreutz, Wolfgang Neuwirth, and Werner Pietsch
Erstes Physikalisches Institut, Universität zu Köln, 5000 Köln, Federal Republic of Germany

(Received 30 June 1980)

The experimental values of electronic stopping cross sections of Li projectiles measured in many organic substances are analyzed with regard to the influence of bonding on the stopping cross section. The invalidity of Bragg's rule, especially for low-velocity projectiles, demands a concept for the analysis which goes beyond simply dividing molecular stopping cross sections into the atomic stopping cross sections of the constituents. Two different approaches are discussed. In the first one, the organic molecule is decomposed into characteristic molecular groups and their corresponding contributions to the molecular stopping cross sections are derived by using only symmetry arguments. The influence of bonding is already included in these values and the problematic atomic stopping cross sections are thus avoided. The second approach, which is more restricted, treats the various bonds in a molecule separately with respect to their specific contributions to the molecular stopping cross section. The results obtained with both procedures are tested by using these values to calculate stopping cross sections of more complex organic compounds. The comparison with measured values shows excellent agreement.

I. INTRODUCTION

In the electronic slowing down of swift particles in matter there is experimental evidence that a simple additivity rule for the stopping cross section measured in a composite target does not exist, especially near and below the maximum of the stopping power. The experimental findings of many investigations connected with the problem of the validity or invalidity of Bragg's rule[1] are displayed in Table I. The situation shown there seems rather conflicting at a first glance: In some cases it is stated that Bragg's rule is valid, in other cases more or less strong deviations from additivity have been observed. The only conclusion which can be drawn from this is that, if in some cases clear evidence is found for a violation of Bragg's rule, this rule cannot be valid in general. This implies that the mutual interaction between the atoms in a compound influences their contribution to the stopping cross section. This raises several questions: Do atomic stopping cross sections still remain meaningful quantities in a composite target, in spite of the sharing of valence electrons among the bonding partners? Is it possible to define atomic stopping cross sections in a composite target so that the derived stopping cross section of a given atom in one target can be used to deduce stopping cross sections of other atoms in another target? Is it further possible to determine quantitatively the influence of the bonding between the atoms on their stopping cross section?

For a closer examination of these problems let us go back to the definition of stopping cross sections. The prime measured quantity in the slowing down of particles in matter is the differential energy loss dE/ds of the projectile. If the target contains a unique type of constituent, it is reasonable to normalize the differential energy loss on the number density n of these constituents

$$S=\frac{1}{n}\frac{dE}{ds}\,; \tag{1}$$

this quantity is called the stopping cross section of the constituent. In a target composed of a single element, these constituents are the atoms themselves, and S is the stopping cross section of one atom in that target. In a target containing several elements, its constituents coincide with the molecules in a gas target, whereas in a crystal, where no separate molecules exist, the smallest units which can be formed with these atoms in accordance with the stoichiometry can be regarded as its constituents. The stopping cross section of such a stoichiometric unit is thus uniquely defined for any target with well-defined stoichiometry.

The questions raised above are concerned with the problem of how to derive a well-defined stopping cross section of such a stoichiometric unit. The simplest possibility for such a decomposition is to treat the atoms for such a stoichiometric unit independent from each other with respect to their contribution to the stopping cross section of the compound. The stopping cross section of a stoichiometric unit can then be written as

$$S(\text{compound})=\sum_i \nu_i S_i(\text{atom})\,, \tag{2}$$

where S_i(atom) is the partial stopping cross section of an atom of element i and ν_i its frequency in the stoichiometric unit. This is Bragg's rule as it is formulated today.

The experimental results show, however, that this is not a good approximation, especially for

TABLE I. Synopsis of experiments related to Bragg's rule.

Authors	Projectile, energy (MeV)	Targets	Result concerning Bragg's rule	Experimental accuracy (%)
Bragg and Kleeman[a]	α, Ra source	Various targets	Bragg's rule	
Förster[b]	α, Rn source	$2H_2 + O_2$, $2H_2O$	Different air equivalent	1
Wenzel and Whaling[c]	p, 0.02–0.54	D_2O ice	$S_{\text{solid}} > S_{\text{vapor}}$	4
Reynolds, Dunbar, Wenzel and Whaling[d]	p, 0.03–0.6	Several hydrocarbons NO, N_2O, NH_3, H_2O, etc.	Deviations below 150 keV	2–4
Palmer[e]	α, 2–8.8	C_2H_5OH, CCl_4, H_2O	$S_{\text{liquid}} < S_{\text{vapor}}$	2
Park and Zimmerman[f]	p,α, 0.04–0.25	Several hydrocarbons	Deviations below 150 keV	1.5–4
Sautter and Zimmerman[g]	p,α, 0.03–0.35	Carbon, two hydrocarbon polymers	Deviations	2–4
Park[h]	α, 0.04–0.2	Several hydrocarbons	Small deviations	2–6
Palmer[i]	α, 1–8.8	Many hydrocarbons	No deviations	2–5
Bourland, Chu, and Powers[j]	α, 0.3–2	Several hydrocarbons CO, CO_2, N_2, N_2O, etc.	Deviations for triple bonded carbon and nitrogen only	1–2
Thompson and Mackintosh[k]	α, 0.3–1.7	Si, SiO_2	Deviations	2–3
Powers, Chu, Robinson, and Lodhi[l]	α, 0.3–2	Many halogen hydrocarbons	Deviations for double and triple bonded carbon	1–2
Feng, Chu, and Nicolet[m]	α, 0.5–2.25	Alloys, metal oxides	No deviations (inconsistency ascribed to errors, not to a violation of Bragg's rule)	2–5
Baglin and Ziegler[n]	α, 2	Many metals and metal-nonmetal compounds	No deviations	2
Feng, Chu, and Nicolet[o]	α, 1–2	Several metal oxides	No deviations for metals, deviation for oxygen	2
Lodhi and Powers[p]	α, 0.3–2	C_3H_8, C_4H_{10}, C_4H_6, C_3H_4, $C_2H_2F_2$, $C_2H_4F_2$	Deviations for double bonded carbon	1
Neuwirth, Pietsch, Hauser, and Richter[q]	Li, 0.1–0.8	Many boron compounds	Large deviations	1
Langley and Blewer[r]	p,α, 0.3–2.5	Er, Er_2O_3	Velocity dependent deviations	2
Matteson, Chau, and Powers[s]	α, 0.3–2	Bulk graphitic carbon, vapor deposited carbon	$S(C_{\text{bulk}}) > S(C_{\text{depos}})$	1–2
Matteson, Powers, and Chau[t]	α, 0.3–2	H_2O ice and vapor	$S_{\text{vapor}} > S_{\text{ice}}$	1–4[u]
Chau, Brown, Lodhi, Powers, Matteson, and Eisenbarth[v]	α, 0.3–2	CH_3OH, C_2H_5OH, C_3H_7OH, $(CH_3)_2O$, $(C_2H_5)_2O$	Deviations for oxygen	1
Thorngate[w]	p, 0.05–0.15	Several hydrocarbons	Deviations	2–3

[a] Reference 1.

[b] M. Förster, Ann. Phys. (Leipzig) 27, 373 (1936).

[c] W. A. Wenzel and W. Whaling, Phys. Rev. 87, 499 (1952).

[d] H. K. Reynolds, D. N. F. Dunbar, W. A. Wenzel, and W. Whaling, Phys. Rev. 92, 742 (1953).

[e] R. B. J. Palmer, Proc. Phys. Soc. 78, 766 (1961).

[f] J. T. Park and E. J. Zimmerman, Phys. Rev. 131, 1611 (1963).

[g] C. A. Sautter and E. J. Zimmerman, Phys. Rev. 140, A490 (1965).

[h] J. T. Park, Phys. Rev. 138, A1317 (1965).

[i] R. B. J. Palmer, Proc. Phys. Soc. 87, 681 (1966).

[j] P. D. Bourland, W. K. Chu, and D. Powers, Phys. Rev. B 3, 3625 (1971); P. D. Bourland and D. Powers, *ibid.* 3, 3635 (1971).

[k] D. A. Thompson and W. D. Mackintosh, J. Appl. Phys. 42, 3969 (1971).

[l] Reference 5.

[m] J. S.-Y. Feng, W. K. Chu, and M-A. Nicolet, Thin Solid Films 19, 227 (1973).

[n] J. E. E. Baglin and J. F. Ziegler, J. Appl. Phys. 45, 1413 (1974).

[o] J. S.-Y. Feng, W. K. Chu, and M-A. Nicolet, Phys. Rev. B 10, 3781 (1974).

[p] Reference 6.

[q] W. Neuwirth, W. Pietsch, K. Richter, and U. Hauser, Z. Phys. A 275, 209 (1975); 275, 215 (1975); W. Pietsch, U. Hauser, and W. Neuwirth, Nucl. Instrum. Methods 132, 79 (1976).

[r] R. A. Langley and R. S. Blewer, Nucl. Instrum. Methods 132, 109 (1976).

[s] S. Matteson, E. K. L. Chau, and D. Powers, Phys. Rev. A 14, 169 (1976).

TABLE I. (*Continued.*)

[t] S. Matteson, D. Powers, and E. K. L. Chau, Phys. Rev. A 15, 856 (1977).

[u] The error is 1% for vapor and 4% for ice.

[v] E. K. L. Chau, R. B. Brown, A. S. Lodhi, D. Powers, S. Matteson, and S. R. Eisenbarth, Phys. Rev. A 16, 1407 (1977).

[w] Reference 7.

low projectile velocities. A next step in the approximation could be, to consider the fact that many properties of a free atom change, if it becomes part of a compound, and consequently to allow for a change in the stopping cross section. This can be formulated as

$$S(\text{atom})_{\text{compound}} = S(\text{atom})_{\text{free}} + \Delta S\,, \tag{3}$$

where $S(\text{atom})_{\text{free}}$ is the stopping cross section of the free atom. The combined influence of all bonds of the atom on its stopping cross section is included in ΔS. This quantity is thus a sum of several contributions, depending on the number and nature of the bonds involved.

A modified Bragg's rule follows then from Eqs. (2) and (3):

$$S(\text{compound}) = \sum_i \nu_i S_i(\text{atom})_{\text{free}} + \sum_i \nu_i \Delta S_i\,. \tag{4}$$

Even in the most favorable case, where, besides the molecular stopping cross section, all stopping cross sections of the free atoms are known, Eq. (4) will give only a value for the combined influence of the bonds on the molecular stopping cross section. The individual contributions to the second sum in Eq. (4) cannot be determined separately.

For lack of experimental stopping cross sections of free atoms, many of the data cited in Table I were evaluated with stopping cross sections measured in solid or molecular gas targets of the elements. This introduces a further uncertainty in the analysis, because extra terms due to the bonds in these targets are involved. Consequently, an analysis based on Bragg's rule even in its modified form [Eq. (4)] cannot yield the quantitative influence of the bonds on the individual stopping cross sections. There is, furthermore, the possibility that the various influences of the bonds involved in this kind of analysis may almost cancel each other so that a validity of Bragg's rule may be simulated. So the notion of atomic stopping cross sections should only be used with caution.

Only in a few cases is it possible to derive stopping cross sections of bound atoms, namely, in solid or gaseous targets of the elements. No other stopping cross sections are needed here for the evaluation and all atoms are equivalent. But these stopping cross sections are only valid for the given bond states of these atoms, and therefore generally only for this special target. Small molecules composed of different atoms, like CO, H_2O, or CH_4, should not be divided further in order to derive atomic stopping cross sections for carbon, oxygen, or hydrogen. The bond structure of carbon in CO is very different from that in CH_4 due to the different types and numbers of the bonding partners.

We present in this paper a new concept for the analysis of molecular stopping cross sections, which accounts for the specific bond structure. It will be shown that with a few restrictive conditions, a decomposition of molecular stopping cross sections can be performed:

$$S(\text{molecule}) = \sum_i S_i(\text{group})\,. \tag{5}$$

The $S_i(\text{group})$ are the partial stopping cross sections of characteristic molecular groups, which form that molecule. They contain a certain number of atoms and their respective bonds, thus including the specific bond structure of the atoms. Equation (5) can be regarded as an additivity rule, not for atoms (Bragg's rule), but for characteristic molecular groups.

This analysis is performed in Sec. II A for organic compounds; because a large number of different molecules are composed of only a small number of different characteristic groups. The experimental values of the stopping cross sections are taken from Ref. 2, and were measured for Li projectiles in the energy range between 200 and 840 keV and are given there for Bohr's velocity ($v_B = e^2/\hbar = 2.19\times10^6$ m/s). All numerical values in this paper are valid for Li projectiles at Bohr's velocity for the molecules in the liquid state.

In Sec. II B it is shown that under some more restrictive conditions a more refined decomposition of molecular stopping cross sections is possible by assuming that the electrons in the bonds contribute independently to the molecular stopping cross section. The results obtained in Secs. II A and II B are tested in Sec. III by using them to calculate stopping cross sections of more complex organic molecules for a comparison with the measured values.

II. ANALYSIS OF STOPPING CROSS SECTIONS OF ORGANIC MOLECULES

A. Basic molecular groups

It is appropriate to start the analysis with the simplest series of organic compounds, namely, the *n*-alkane molecules, which contain only carbon and hydrogen atoms. Their characteristic feature is an unbranched chain of carbon atoms. Each hydrogen atom is always bound to a carbon atom, but there are three different types of carbon atoms with regard to their bond structure: (i) A carbon atom with four hydrogen atoms as nearest neighbors, which occurs, however, only in methane, (ii) carbon atoms with single bonds to three hydrogen atoms and one carbon atom form the ethane molecule and are always the first and the last carbon atom in the chains of the higher *n*-alkanes, and (iii) carbon atoms with single bonds to two hydrogen and two carbon atoms are located within the chains and occur for the first time in *n*-propane. Carbon atoms with three or even four carbon atoms as nearest neighbors are found, e.g., in hydrocarbons with branched chains.

Such a characterization of the atoms accounts for the difference in the bonds to their nearest neighbors only. A much more complicated situation arises if the total bond structure is taken into account, because then the number of different carbon atoms increases considerably. In *n*-decane with ten carbon atoms, for example, the carbon atoms nos. 1 and 10, 2 and 9, etc., are equal in their bond structure, but the carbon atom no. 2 differs from nos. 1, 3 to 8, and 10. So there are altogether five different carbon atoms in *n*-decane with respect to their whole environment. Under these aspects it is not even possible to compare carbon atoms from different molecules of the same series, because there exist no equivalent carbon atoms in the different members of the series. It is therefore necessary to make an assumption to enable an analysis. The most obvious first-order approach is to characterize the atoms according to the bonds to their nearest neighbors only. Consequently, the *n*-alkanes (except the two lowest ones) contain one type of hydrogen atom always bound to a carbon atom, and two different carbon atoms, namely, either bound to three hydrogen and one carbon atom (the first type), or bound to two hydrogen and two carbon atoms (the second type).

Following for the moment the usual concept of decomposing molecular stopping cross sections into atomic stopping cross sections, but considering now the different types of carbon atoms, we can write the stopping cross section of a *n*-alkane molecule with ν carbon atoms as

$$S_\nu = (2\nu + 2)s(\mathrm{H}) + 2s(\mathrm{C}_1) + (\nu - 2)s(\mathrm{C}_2)\,, \quad \nu \geq 2 \qquad (6)$$

where $s(\mathrm{H})$ is the contribution of the H atom to the molecular stopping cross section and $s(\mathrm{C}_1)$ and and $s(\mathrm{C}_2)$ are those of the first and second type of C atoms, respectively. The difference between the stopping cross sections of any two *n*-alkane molecules is

$$S_\mu - S_\nu = 2(\mu - \nu)s(\mathrm{H}) + (\mu - \nu)s(\mathrm{C}_2)\,. \qquad (7)$$

This shows that the whole set of equations, which can be formed with the measured values S_ν of the *n*-alkane molecules contains only two linearly independent equations so that the three unknown quantities $s(\mathrm{H})$, $s(\mathrm{C}_1)$, and $s(\mathrm{C}_2)$ cannot be determined, independent of the number of measured molecular stopping cross sections. Additionally, there still remains the problem of how to treat the electrons shared among the atoms in the bonds. This problem is not only connected with a possible asymmetric distribution of the electrons in the bonds, but also with the fact that the valence electrons are in completely different states compared with those in free atoms. But an analysis with molecular stopping cross sections as the only given quantities can only be performed by dividing bonds, and this must be done in such a way that no ambiguity will be introduced due to the partitions of the bonds. This can be achieved by observing the following rules: A bond between different types of atoms must not be divided and a bond between two atoms of the same kind can be divided uniquely because of symmetry. This symmetry can be distorted, however, for instance if an adjacent bond is polar (hyperconjugation).

According to these considerations, the H atoms in the *n*-alkanes must not be separated from the C atoms, as was done above in the formal definition of the stopping cross sections $s(\mathrm{H})$, $s(\mathrm{C}_1)$, and $s(\mathrm{C}_2)$. The C–C bonds, on the other hand, can be divided uniquely, as no strong polar bonds exist in the *n*-alkanes. A decomposition of the molecular stopping cross sections of the *n*-alkanes can be performed in this approximation by using only the symmetry in the bonds between the carbon atoms. The smallest units are now not atoms but groups of atoms, each containing a well-defined fraction of the valence electrons, i.e., the bonds, see Fig. 1(a). An *n*-alkane molecule with ν carbon atoms is thus composed of two CH_3 groups, each bound to one carbon atom and containing three C–H bonds and one-half of a C–C bond, and ν-2 CH_2 groups bound to two carbon atoms, each with two C–H bonds and twice one-half of a C–C bond. These two types of molecular groups account quite naturally for the different bond structure of the carbon atoms in the *n*-alkanes.

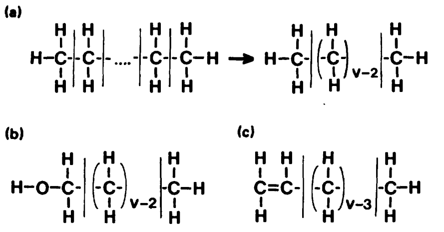


FIG. 1. The characteristic molecular groups of (a) *n*-alkane molecules, (b) 1-alcohol molecules, and (c) 1-alkene molecules. A short dash symbolizes one-half of a C–C bond, ν is the number of carbon atoms.

The electronic structure of the CH_2 or CH_3 groups does not depend on the farther molecular environment in this approximation so that the stopping cross section of an *n*-alkane molecule with $\nu \geq 2$ carbon atoms is given by

$$S_\nu(n\text{-alkane}) = 2s(CH_3) + (\nu - 2)s(CH_2)\,, \tag{8}$$

where $s(CH_2)$ and $s(CH_3)$ are now the contributions of the respective groups to the molecular stopping cross section. The difference between any two *n*-alkane molecules is just proportional to the stopping cross section of the CH_2 group (bound to two carbon atoms)

$$S_\mu - S_\nu = (\mu - \nu)s(CH_2)\,. \tag{9}$$

The stopping cross sections of molecules of related series like the 1-alkenes and the 1-alcohols can be analyzed in a similar way, see Figs. 1(b) and 1(c). Two additional groups are in these molecules, namely, the $HC{=}CH_2$ group bound to one carbon atom in the 1-alkenes, and the CH_2OH group in the 1-alcohols. The CH_2 group next to the OH group in the alcohols must be treated differently from the inner CH_2 groups because of its different bond structure. Its C atom is—apart from the two H atoms—not bound to two C atoms but to one C and one O atom. The strong polarity in the C–O–H bonds even forbids the separation of this CH_2 group. The $HC{=}CH_2$ group contains another CH_2 group, which has a C atom bound to two H atoms and to one C atom in a C=C double bond.

The molecular stopping cross sections of the 1-alkenes and the 1-alcohols are then

$$S_\nu(1\text{-alkene}) = s(HC{=}CH_2) + s(CH_3) + (\nu - 3)s(CH_2)\,, \quad \nu \geq 3 \tag{10}$$

and

$$S_\nu(1\text{-alcohol}) = s(CH_2OH) + s(CH_3) + (\nu - 2)s(CH_2)\,, \quad \nu \geq 2\,. \tag{11}$$

The difference between any two members of each series is again given by Eq. (9).

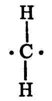
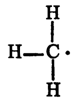
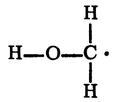
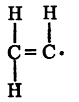
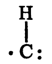
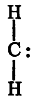
The experimental data[2] for these three series can be used for a linear-regression fit of the molecular stopping cross sections as a function of the number ν of carbon atoms. The slope corresponds in all cases to the stopping cross section of the CH_2 group bound to two carbon atoms. The intercept at $\nu = 2$ yields $2s(CH_3)$ for the *n*-alkanes and $s(CH_3) + s(CH_2OH)$ for the 1-alcohols. The intercept at $\nu = 3$ gives $s(CH_3) + s(HC{=}CH_2)$ for the 1-alkenes. The results are listed in Table II. The three slopes agree within the limits of error. This shows that the influence of the wider environment of a CH_2 group on its stopping cross section can, in fact, be neglected within the accuracy of the data. The average value of 63.4 ± 0.3 a.u. can be regarded as the contribution of the CH_2 group, bound to two carbon atoms, to the stopping cross section of organic molecules (in the liquid state) for Li projectiles at Bohr's velocity. This adopted value of the stopping cross section of the CH_2 group is now inserted in Eqs. (8), (10), and (11). This gives a set of values of the stopping cross section of the CH_3 group from Eq. (8), their average is then the adopted value of $s(CH_3)$. With this value we calculate the stopping cross sections of the $HC{=}CH_2$ and CH_2OH groups using Eqs. (10) and (11), respectively. The results are listed in Table III.

The CH_2 group bound to two carbon atoms in chainlike organic compounds has a tetrahedral bond structure with an angle of 109° between neighboring bonds. Deviations from this structure occur if the CH_2 group is part of a molecule with a closed structure, like the cycloalkanes as, e.g., cyclohexane in Fig. 2(a). The molecules of this

TABLE II. Parameters of the linear-regression fit of the stopping cross sections of different hydrocarbon series in a.u. for Li projectiles at Bohr's velocity ($E_{Li} = 175$ keV, 1 a.u. $= 0.762 \times 10^{-15}$ eV cm^2, ν is the number of carbon atoms).

Series	Region of fit	Slope $s(CH_2)$	Intercept
n-alkanes	$\nu = 5$–14	63.2 ± 0.3	$\nu = 2$: 156.0 ± 2.0
1-alkenes	$\nu = 5$–8, 10	63.5 ± 0.4	$\nu = 3$: 196.6 ± 1.7
1-alcohols	$\nu = 3$–11	63.4 ± 0.3	$\nu = 2$: 184.6 ± 1.4

TABLE III. Derived stopping cross sections of molecular groups in a.u. for Li projectiles at Bohr's velocity ($E_{Li} = 175$ keV, 1 a.u.$= 0.762 \times 10^{-15}$ eV cm^2).

Molecular group Structure [a]	Description	Stopping cross section
 $\cdot\overset{H}{\underset{H}{C}}\cdot$	CH_2 group bound to two C atoms	63.4 ± 0.3
 $H-\overset{H}{\underset{H}{C}}\cdot$	CH_3 group bound to one C atom.	77.4 ± 0.7
 $H-O-\overset{H}{\underset{H}{C}}\cdot$	CH_2OH group bound to one C atom	107.2 ± 1.2
 $\underset{H}{\overset{H}{C}}=\overset{H}{C}\cdot$	$HC=CH_2$ group bound to one C atom	119.6 ± 1.2
 $\cdot\overset{H}{C}:$	CH group in cycloalkenes	52.3 ± 1.0
 $\overset{H}{\underset{H}{C}}:$	CH_2 group in double bond to one C atom	67.2 ± 1.6

[a] The symbols mean: (—) full single bond, (·) one-half of a single bond, (=) full double bond, (:) one-half of a double bond.

series contain only CH_2 groups but the bond angles deviate from the tetrahedral value as a consequence of the ringlike formation. These deviations are due to so-called ring strains, which depend on the number of carbon atoms. These ring strains are large in molecules with a small number of carbon atoms and decrease with increasing number of carbon atoms.[3] The distribution of the electrons in the bonds is, in general, influenced by these strains as can be seen, e.g., in the behavior of the mean binding energy of the CH_2 group in ringlike compounds.[4] In principle, there must also be an influence on the stopping cross sections of these molecules. This was tested for the cycloalkanes with five to eight carbon atoms, by deriving the mean contribution of their CH_2 groups to the stopping cross section. This is simply done by dividing the measured molecular stopping cross sections[2] by the number of carbon atoms. The results are listed in Table IV. These values, except that of cyclopentane, agree within the limits of error with the average value of the CH_2 group in chainlike compounds. But the deviation for cyclopentane is not significant enough to allow further conclusions to be drawn. The stopping cross sections of cyclopropane and cyclobutane, which have much stronger ring strains, could at present not be measured with our method, as it works only with solid or liquid target substances[2] and the apparatus is not yet equipped with a cryostat for li-

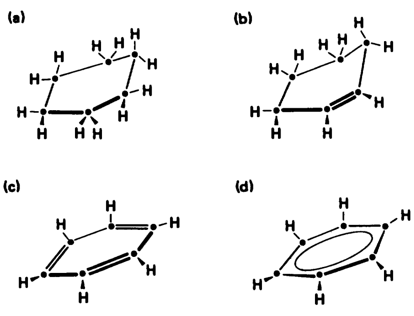


FIG. 2. Structure of (a) cyclohexane, (b) cyclohexene, (c) benzene (Kekulé formula), and (d) benzene with completely delocalized π electrons. Full circles represent the carbon atoms.

TABLE IV. Mean values of the stopping cross section of the CH_2 group in cycloalkanes in a.u. for Li projectiles at Bohr's velocity (E_{Li} = 175 keV, 1 a.u. = 0.762 $\times 10^{-15}$ eV cm^2).

Cycloalkane	Mean value $s(CH_2)$
Cyclopentane	64.2 ± 0.4
Cyclohexane	63.7 ± 0.4
Cycloheptane	63.1 ± 0.5
Cyclooctane	63.4 ± 0.5

quifying gases.

The stopping cross section of another molecular group can be determined from the data of the cycloalkenes, see, e.g., cyclohexene in Fig. 2(b). Each molecule of this series contains two CH groups each with one C–H bond, one-half of a C–C single bond, and one-half of a C=C double bond. The division of the C=C bond is possible, too, because of the same symmetry argument used above for the C–C bonds. The stopping cross section of this CH group was derived by using for each cycloalkene the value of the CH_2 group from the corresponding cycloalkane. These derived values for the CH group are listed in Table V. They agree with each other within their errors, in spite of different ring strains. Their average value of 52.3 ± 1.0 a.u., which is also listed for comparison in Table III, is the adopted value of the stopping cross section of the CH group in cycloalkenes.

This value can be compared with one-sixth of the molecular stopping cross section of benzene.[2] The benzene molecule is composed of six identical CH groups, which are in the most simple approximation of completely localized electrons [Kekulé formula, see Fig. 2(c)], identical with the CH group in cycloalkenes. The mean contribution of the CH group to the molecular stopping cross section of benzene is 52.3 ± 0.4 a.u., in good agreement with the value of the CH group in cycloalkenes. With regard to the stopping cross section, there is—within the accuracy of the data—no difference between the CH group in cycloalkenes and that in benzene. Nevertheless, both groups are different, because the double bond in the cycloalkenes is localized, whereas a more accurate description of the benzene molecule considers a complete delocalization of the π valence electrons, see Fig. 2(d). The data show, however, that the influence of the delocalization of the electrons in the carbon ring bonds on the molecular stopping cross section is at most 1%.

TABLE V. Derived values of the stopping cross section of the CH group in cycloalkenes in a.u. for Li projectiles at Bohr's velocity (E_{Li} = 175 keV, 1 a.u. = 0.762 $\times 10^{-15}$ eV cm^2).

Cycloalkene	Derived value s(CH)
Cyclopentene	53.0 ± 1.6
Cyclohexene	51.6 ± 1.3
Cyclooctene	52.4 ± 1.9

The $HC=CH_2$ group contains the CH group (with one-half of a C–C single bond and one-half of a C=C double bond) as a subunit. This gives the stopping cross section of the CH_2 group bound to one carbon atom in a C=C double bond; its value is 67.2 ± 1.6 a.u. (last entry in Table III). This can be compared with the value of the CH_2 group bound in single bonds to two C atoms. The difference of 3.9 ± 1.6 a.u. is obviously caused by the difference in the bond structure, i.e., twice one-half of a C–C single bond (i.e., one full C–C bond) for the first, and one-half of a C=C double bond for the second group. This behavior of a C=C double bond has been noticed[5-7] already; there, however, the molecular stopping cross sections have been analyzed by deriving atomic stopping cross sections.

B. Independent bond approximation

The derivation of stopping cross sections of molecular groups in the preceding subsection is based on symmetry arguments concerning the sharing of valence electrons among the atoms of a molecule, but—as a first-order approach—only with respect to the two atoms forming that bond. Any disturbing influence on its symmetry cannot be separated and leads to the formation of larger groups containing this influence, e.g., the CH_2OH group in alcohols.

The n-alkane molecules contain in this sense only two different types of bonds; the C–H and the C–C bonds. This suggests an analysis of molecular stopping cross sections by introducing partial contributions of specific bonds. If it is assumed that the electrons of an atom or a compound behave independently from each other with respect to the inelastic processes which determine the electronic stopping cross sections, then the stopping cross section of an atom or a molecule can be composed of contributions of individual electrons. These contributions depend nevertheless on all the other electrons as the state of a given electron is determined by the total electronic configuration of an atom or a compound.

It is appropriate to treat the valence electrons separately from the core electrons in the evaluation of molecular stopping cross sections and it is also justified to regard bonds formed by the same type and number of valence electrons as equal with respect to their contribution to the molecular stopping cross section. Then we can write the stopping cross section of a molecule containing M types of different bonds, each occuring m_i times, and N types of different atoms, each occuring n_j times, as

$$S(\text{molecule}) = \sum_{i=1}^{M} m_i \sigma_i + \sum_{j=1}^{N} n_j \rho_j \,, \tag{12}$$

where σ_i is the contribution of the electrons in the bond of type i and ρ_j is the contribution of the core electrons of the atom of type j.

This treatment is analogous to the separation of several molecular properties in partial contributions, which remain additive, if they are applied to other molecules. Such a quantity is, for instance, the molecular electric polarizability,[8,9] which can be described by Eq. (12), provided σ_i and ρ_j are replaced by the bond or core polarizabilities, respectively. A similar description also exists for the diamagnetic susceptibility of molecules.[10] Although these quantities are not directly related with stopping cross sections, they have one thing in common, as they depend directly on the electronic distribution in the atomic or molecular orbitals.

For the procedure described by Eq. (12), the n-alkane molecules are the simplest ones, as they contain only two different bonds ($M=2$), and only two different atoms ($N=2$). The application of Eq. (12) to the n-alkane molecule with ν carbon atoms leads to

$$S_\nu(n\text{-alkane}) = (2\nu+2)\sigma(\text{C--H}) + (\nu-1)\sigma(\text{C--C}) + \nu\rho(\text{C}) \tag{13}$$

and

$$S_\mu - S_\nu = 2(\mu-\nu)\sigma(\text{C--H}) + (\mu-\nu)\sigma(\text{C--C}) + (\mu-\nu)\rho(\text{C})\,. \tag{14}$$

$\sigma(\text{C--H})$ is the contribution of a C–H bond formed by one 1s electron of hydrogen and one sp^3 electron of carbon, $\sigma(\text{C--C})$ corresponds to the two sp^3 electrons forming the C–C bond, and $\rho(\text{C})$ is the contribution of the two 1s core electrons of the carbon atom. As the 1s electron of the hydrogen atom participates in the bond, there is no remaining core contribution of hydrogen, i.e., $\rho(\text{H})=0$.

This decomposition leads to three unknown quantities for a set of equations containing again only two linearly independent ones. But the binding energy of a 1s electron of carbon is about 10 hartrees, whereas the kinematic limit of energy transfer is only 2 hartrees in an ion-electron collision at Bohr's velocity (neglecting the momentum distribution of the bound electron). This gives a rather strong argument that the 1s core electrons of carbon contribute much less to the stopping cross section than the valence electrons. This argument will not hold for atoms with a more complicated core.

For the determination of the contributions of the bonds from the measured n-alkane stopping cross sections, we can refer to the derived stopping cross sections of molecular groups in Table III, because all bonds of the same type were already treated as equal in the derivation of the stopping cross sections of these groups. This gives

$$\begin{aligned} s(\text{CH}_2) &= 2\sigma(\text{C--H}) + 2\{\tfrac{1}{2}\sigma(\text{C}-\text{C})\} + \rho(\text{C}) \\ &= 2[\sigma(\text{C--H}) + \tfrac{1}{4}\rho(\text{C})] + [\sigma(\text{C--C}) + \tfrac{1}{2}\rho(\text{C})] \end{aligned} \tag{15}$$

and

$$\begin{aligned} s(\text{CH}_3) &= 3\sigma(\text{C--H}) + \tfrac{1}{2}\sigma(\text{C--C}) + \rho(\text{C}) \\ &= 3[\sigma(\text{C--H}) + \tfrac{1}{4}\rho(\text{C})] + \tfrac{1}{2}[\sigma(\text{C--C}) + \tfrac{1}{2}\rho(\text{C})]\,. \end{aligned} \tag{16}$$

These equations can be solved for the quantities in square brackets[11] with the values of $s(\text{CH}_2)$ and $s(\text{CH}_3)$ in Table III, and give (in a.u.),

$$[\sigma(\text{C--H}) + \tfrac{1}{4}\rho(\text{C})] = 22.9 \pm 0.4 \tag{17}$$

and

$$[\sigma(\text{C--C}) + \tfrac{1}{2}\rho(\text{C})] = 17.6 \pm 0.7\,. \tag{18}$$

This clear difference between the contribution of the two valence electrons in these bonds reflects the difference in the electronic distribution of the C–H and the C–C bonds. If a nonnegligible contribution $\rho(\text{C})$ exists, this would only change the absolute values in the same sense, it would even enlarge the difference in the contributions of the valence electrons.

The stopping cross section of the $\text{HC}{=}\text{CH}_2$ group can be evaluated in a similar way

$$\begin{aligned} s(\text{HC}{=}\text{CH}_2) &= 3\sigma(\text{C--H}) + \tfrac{1}{2}\sigma(\text{C--C}) + \sigma(\text{C}{=}\text{C}) + 2\rho(\text{C}) \\ &= 3[\sigma(\text{C--H}) + \tfrac{1}{4}\rho(\text{C})] + \tfrac{1}{2}[\sigma(\text{C--C}) + \tfrac{1}{2}\rho(\text{C})] \\ &\quad + [\sigma(\text{C}{=}\text{C}) + \rho(\text{C})]\,, \end{aligned} \tag{19}$$

where $\sigma(\text{C}{=}\text{C})$ is correspondingly the contribution of the four valence electrons of the two carbon atoms forming the C=C bond. With the value for $s(\text{HC}{=}\text{CH}_2)$ of Table III and the values of Eqs. (17) and (18) we obtain (in a.u.)

$$[\sigma(\text{C}{=}\text{C}) + \rho(\text{C})] = 42.2 \pm 1.6\,. \tag{20}$$

The four valence electrons in the C=C double bond (two in an sp^2 σ bond and two in a p π bond) obviously give a larger contribution to the stopping cross section than four sp^3 electrons in two C–C single

TABLE VI. Derived contributions of various bonds occuring in hydrocarbon compounds to the stopping cross sections (in a.u.) for Li projectiles at Bohr's velocity ($E_{\mathrm{Li}} = 175$ keV, 1 a.u. $= 0.762 \times 10^{-15}$ eV cm^2).

	Atomic orbitals forming the bond	Derived contribution of the bond
$[\sigma(\mathrm{C-H}) + \frac{1}{4}\rho(\mathrm{C})]$	1s(H) and sp^3(C)	22.9 ± 0.4
$[\sigma(\mathrm{C-C}) + \frac{1}{2}\rho(\mathrm{C})]$	two sp^3(C)	17.6 ± 0.7
$[\sigma(\mathrm{C=C}) + \rho(\mathrm{C})]$	two $sp^2(\sigma)$ and two $p(\pi)$ of C	42.2 ± 1.6

bonds. The difference is (in a.u.)

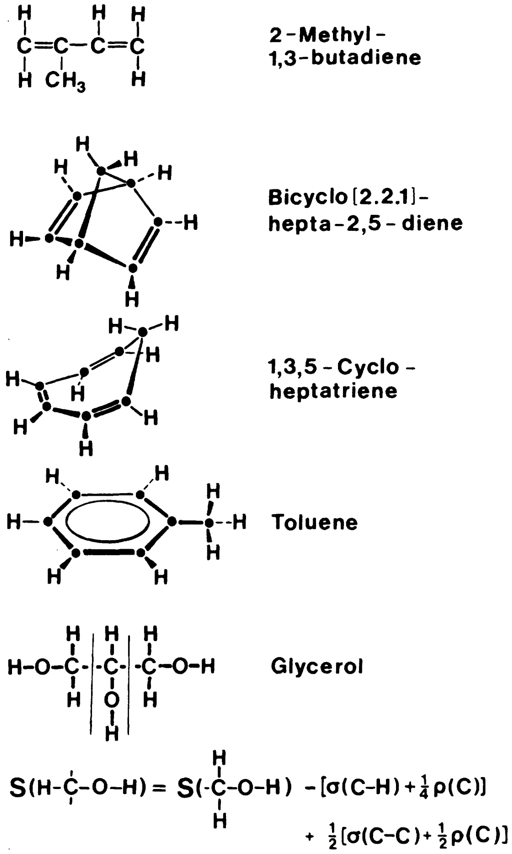
$$\begin{aligned}\Delta\sigma &= [\sigma(\mathrm{C{=}C}) + \rho(\mathrm{C})] - 2[\sigma(\mathrm{C-C}) + \tfrac{1}{2}\rho(\mathrm{C})]\\ &= \sigma(\mathrm{C{=}C}) - 2\sigma(\mathrm{C-C})\\ &= 7.0 \pm 2.1\,,\end{aligned} \tag{21}$$

independent of $\rho(\mathrm{C})$. The results are summarized in Table VI. It should be pointed out that they represent average values obtained from the measured molecular stopping cross sections of many n-alkane and 1-alkene molecules.

In summary, we stress that the concept of independent bonds is more restricted than the concept of independent molecular groups. It should not be used in cases where neighboring bonds influence each other, causing so-called hyperconjugation effects, which is certainly the case if strong polar bonds are present. In the general case, it is more favorable to derive stopping cross sections of characteristic molecular groups, which already contain two or more bonds and their mutual influence.

III. EMPIRICAL PREDICTION OF MOLECULAR STOPPING CROSS SECTIONS

The question of whether such a decomposition of a molecular stopping cross section into contributions of independent bonds is realistic, can be tested by calculating with these data values for the stopping cross sections of other organic molecules. This test is done with molecules of a more complex structure (see Fig. 3) compared with the structure of those molecules, which have been used for the derivation of these values. The results are given in Table VII.



$$S(\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}O{-}H}) = S(\mathrm{{\cdot}\overset{H}{\underset{H}{C}}{-}O{-}H}) - [\sigma(\mathrm{C{-}H}) + \tfrac{1}{4}\rho(\mathrm{C})] + \tfrac{1}{2}[\sigma(\mathrm{C{-}C}) + \tfrac{1}{2}\rho(\mathrm{C})]$$

FIG. 3. Structure of the compounds listed in Table VII. The characteristic groups and bonds used for the calculation of the stopping cross section of glycerol are indicated at the bottom of this figure.

The first three compounds in Table VII contain only C–H, C–C, and C=C bonds so that their molecular stopping cross section can be calculated

TABLE VII. Measured and calculated stopping cross sections in a.u. of some more complex organic compounds for Li projectiles at Bohr's velocity ($E_{\mathrm{Li}} = 175$ keV, 1 a.u. $= 0.762 \times 10^{-15}$ eV cm^2).

Compound	Formula	Stopping cross section measured	calculated
2-methyl-1, 3-butadiene	C_5H_8	300 ± 2	302 ± 4
Bicyclo[2.2.1]hepta-2, 5-diene	C_7H_8	374 ± 4	373 ± 6
1, 3, 5-cycloheptatriene	C_7H_8	379 ± 5	379 ± 6
Toluene	C_7H_8	375 ± 2	377 ± 3
Glycerol	$C_3H_8O_3$	311 ± 2	308 ± 3

using only the values of Table VI. For example, the stopping cross section of C_7H_8 (bicyclo [2.2.1] hepta-2, 5-diene) can be simply expressed as

$$S(C_7H_8) = 8[\sigma(C-H) + \tfrac{1}{4}\rho(C)] + 6[\sigma(C-C) + \tfrac{1}{2}\rho(C)] + 2[\sigma(C=C) + \rho(C)]. \quad (22)$$

The two other values are calculated in a similar way.

The concept of independent bonds can only partially be used for toluene. Here it is more appropriate to use the derived value of the CH group in benzene, because it already contains the possible influence between the carbon ring bonds and the C–H bonds. So the stopping cross section of toluene is calculated in a mixed description:

$$S(\text{toluene}) = 6s(CH)_{\text{benzene}} + [\sigma(C-C) + \tfrac{1}{2}\rho(C)] + 2[\sigma(C-H) + \tfrac{1}{4}\rho(C)]. \quad (23)$$

This formula is not quite correct, as it contains one C–H bond to a C atom with delocalized bonds instead of the C–H bond to a C atom with localized bonds. So the result in Table VII is uncertain just as to the difference between these two contributions, which is certainly small compared with the total molecular stopping cross section.

The concept of independent bonds cannot be used in the case of glycerol, too, because of the three polar groups. To account for this influence we use the stopping cross section of the CH_2OH group derived from the 1-alcohols (Table III). This group exists twice in glycerol, but the middle group differs in the bond structure of the C atom. This is bound to one H and two C atoms, whereas in the two outer groups the C atom is bound to two H atoms and one C atom. The approximation of the contribution of this middle group is explained at the bottom of Fig. 3. This accounts for the bond structure and also as far as possible for the influence of hyperconjugation. The remaining influence of hyperconjugation on the C–H and C–C bonds cannot be considered here, leaving an uncertainty, which is small compared with the total stopping cross section. This can be seen in the good agreement between the measured and calculated stopping cross sections of glycerol.

All calculated values of the stopping cross sections in Table VII show a good agreement with the measured values within about 1%. This means that the contribution of the C–H, C–C, and C=C bonds to the molecular stopping cross sections are largely independent of their position within the molecule. However, a complete decomposition into single bonds is not suitable in cases where a strong influence of hyperconjugation exists, which is quantitatively unknown. This influence can be considered as far as possible by using appropriate molecular groups, which already contain the main influence of hyperconjugation.

IV. CONCLUSION

The molecular stopping cross sections have been discussed on three different levels of approximation.

1. *Independent atoms*. This most simple approximation decomposes the molecular stopping cross section in atomic ones, following the stoichiometric formula of the molecule. This presumes that atomic stopping cross sections remain well-defined quantities also in composite targets, in spite of the different distribution and association of the valence electrons. It is certainly a reasonable approximation if the velocity of the projectile is large compared with the average orbital velocities of the outer electrons (Bethe-Bloch region). This treatment, however, is no longer valid for lower velocities, as here pronounced Z_1 and Z_2 oscillations in the stopping cross sections exist, and deviations from Bragg's rule (which is based on independent atoms) are known. Consequently, the concept of atomic stopping cross sections in compounds cannot be used for the determination and interpretation of chemical binding effects.

2. *Independent groups*. Information about the influence of bonding can only be obtained if the bond structure of the atoms is taken into account. Here it is necessary to dissect the molecule, i.e., to divide bonds. Such a division of bonds is only possible if the electrons in that bond can be uniquely redistributed among the atoms. This can be done if the charge distribution in the bonds is symmetric, and this gives the basis for the partition of a molecule in its characteristic molecular groups.

As the overwhelming number of organic molecules are composed of a very small number of different elements, they contain also a limited number of characteristic groups. The data of the groups derived here can be used to determine those for other relevant groups. A possible application is to predict stopping cross sections of tissue, which can be regarded as a complex formed by such groups. Those data are necessary to calculate the energy deposited in tissue irradiated with charged particles. It is further necessary to investigate molecules with different polar groups to get more information about the influence of polarity and of hyperconjugation on the stopping cross section.

3. *Independent bonds*. A more detailed analysis is possible for compounds containing only carbon

and hydrogen. All electrons, except the two 1*s* electrons of carbon are involved in the C–H, C–C, and C=C bonds of these molecules. The essential assumption in this case is that the contribution of the electrons in these bonds is not only independent of the relative position of the bonds in the molecule, but also independent of neighboring bonds. The latter condition is certainly not valid in regions with strong polar bonds, hence this concept was not used in the analysis of molecules with polar groups. The question of whether this concept can also be used for molecules with more complicated bonds cannot be answered at present because more systematic data are needed.

ACKNOWLEDGMENT

This work was supported by Bundesministerium für Forschung und Technologie.

---

[1] W. H. Bragg and R. Kleeman, Philos. Mag. 10, 318 (1905).

[2] R. Kreutz, W. Neuwirth, and W. Pietsch, Phys. Rev. A 22, 2598 (1980), paper I.

[3] J. March, *Advanced Organic Chemistry, Reactions, Mechanisms, and Structure* (McGraw-Hill Kogakusha, Tokyo, 1968), p. 116.

[4] H. R. Christen, *Grundlagen der Organischen Chemie* (Diesterweg-Salle, Frankfurt am Main, 1975), 3rd ed., p. 111.

[5] D. Powers, W. K. Chu, R. J. Robinson, and A. S. Lodhi, Phys. Rev. A 6, 1425 (1972).

[6] A. S. Lodhi and D. Powers, Phys. Rev. A 10, 2131 (1974).

[7] J. H. Thorngate, Health Phys. 32, 541 (1977).

[8] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 947.

[9] K. G. Denbigh, Trans. Faraday Soc. 36, 936 (1940).

[10] G. Foëx, *Tables de Constantes et Donnees Numeriques* (Masson, Paris, 1957), Vol. 7.

[11] The expressions in square brackets in Eqs. (15)–(23) represent the only grouping of the unknowns σ (C–H), σ(C–C), σ(C=C), and ρ(C), which yields numerical results.