Electron-Impact Studies of Substituted Alkanes[1]

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Abstract: The ionization potentials of several substituted alkanes, in which sulfur or selenium is substituted for one of the carbon atoms and/or amino and/or carboxyl groups are substituted for one or two of the hydrogen atoms, have been measured. The energy requirements for ionization of these complex molecules are compared with the measured ionization potentials of simpler molecules having no or only one substituent. Comparison is also made with values for the ionization potential calculated by a group orbital treamtent.[2,3] The onset potentials for the formation of the major fragment ions have also been measured. A short discussion of the relationship between the intensity of these ions and the energetics of the fragmentation processes is given.

Electron impact has been used to study the ionization potentials of many organic molecules. The results of these studies have been reviewed and tabulated by Kiser[4] and earlier by Field and Franklin.[5] The latter, along with McDowell[6] and Kraus and Dibeler,[7] have discussed critically the interpretation of appearance-potential data and the theoretical treatment of the primary ionization process. Included in these reviews are the results of exacting and systematic studies of homologous series of monosubstituted alkanes (acids, esters, alcohols, amines, ketones, aldehydes, and others). Only one report[8] to date concerns the energetics for the ionization and fragmentation of alkanes having more than a single substituent. The bifunctional molecules, glycine and isoleucine, and the trifunctional molecule, methionine, have been studied.[8] The somewhat crude values reported for their ionization potentials were used as supporting evidence for a proposed unimolecular decomposition.

The purpose of this report is to present the results of a more complete and accurate measurement of the ionization potentials of some polyfunctional alkanes and to compare conclusions derived from the measured values with those reached from values obtained by a group orbital calculation employing a united atom model.[2,3] Franklin[2] has shown that the calculated ionization potentials for all the common monofunctional alkanes agree quite well with the measured values. Favorable comparisons were made for alcohols, ethers, amines, alkyl halides, aldehydes, ketones, acids, and esters. One of the significant assumptions made by Franklin[2] in all these calculations was that the value of the interaction parameter was zero for all interactions except those involving atoms or groups of atoms which are nearest (adjacent) neighbors. From the agreement of the measured and calculated ionization potentials, one concludes that this assumption is apparently correct. If indeed all interactions except those involving nearest neighbors are zero or negligible, one could also assume that the measured ionization potential of a polysubstituted alkane could be accurately estimated from the ionization potentials of monofunctional molecules which have the same or similar carbon skeletons. The measured value should be very close to the critical potential of the monosubstituted alkane which has the lowest ionization potential and should be independent of effects from all other substituents as long as they are not nearest neighbors. Both calculated and measured ionization potentials of mono-, di-, and trifunctional alkanes are compared in this report to test the validity of this hypothesis.

The onset energy potentials required to form the major fragment ions from these complex molecules are also presented. These results are discussed in relation to the probable frequency of selected fragmentations predicted from the observed energy requirements for alternate unimolecular decompositions.

Experimental Section

Instrumentation. A General Electric analytical mass spectrometer was modified and used to establish the mass spectra and secure the ionization efficiency data from which the onset potentials were determined. Gas and liquid samples were introduced from a Microtek universal inlet system. Low vapor pressure solids (all the amino acids) were introduced directly into the ionization chamber using a vacuum lock described previously.[9] The details of the sampling system and the instrumental modifications have already been discussed.[10]

Appearance-Potential Accuracy. All appearance-potential data were obtained with the electron energy calibrating gas (argon or krypton) in the ion chamber simultaneously with the sample under investigation. The accuracy of the onset potentials determined from several different treatments of the ionization efficiency data was checked. The results for argon and krypton, where the difference in ionization potential is accurately known, are given in Table I. The method which seems to yield the most precise and accurate results, especially when the shape of the ionization efficiency curve for the unknown deviates from the general shape for the rare gas, is the direct observation of the vanishing current (direct) as described by Field and Franklin.[11] It has been the authors' experience that this procedure is also the least subjective and least time consuming for determining the difference in the onset potential of the calibrating gas and the unknown. However, no ionization efficiency curves are obtained when this vanishing current (direct) method is used. Because the gross detail of these curves may be of some interest, we have used the ratio extrapolation[12] procedure to

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1945.

(2) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).

(3) G. G. Hall, *Trans. Faraday Soc.*, **49**, 113 (1953); **50**, 319 (1954).

(4) R. W. Kiser, "Tables of Ionization Potentials," USAEC, TID-6142, June 1960.

(5) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, pp 243–310.

(6) C. A. McDowell, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 506–588.

(7) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, pp 117–161.

(8) G. A. Junk and H. J. Svec, *J. Am. Chem. Soc.*, **85**, 839 (1963).

(9) G. A. Junk and H. J. Svec, *Anal. Chem.*, **37**, 1629 (1965).

(10) G. A. Junk and H. J. Svec, presented at the Twelfth Annual Conference on Mass Spectrometry and Allied Topics, Montreal, Canada, June 1964, Paper 84.

(11) Reference 5, p 30.

(12) H. J. Svec and G. D. Flesch, ref 10, Paper 21.

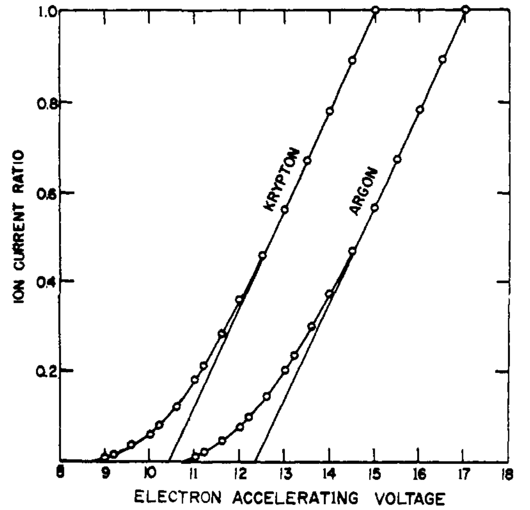

Figure 1. Rare gas ionization efficiency curves.

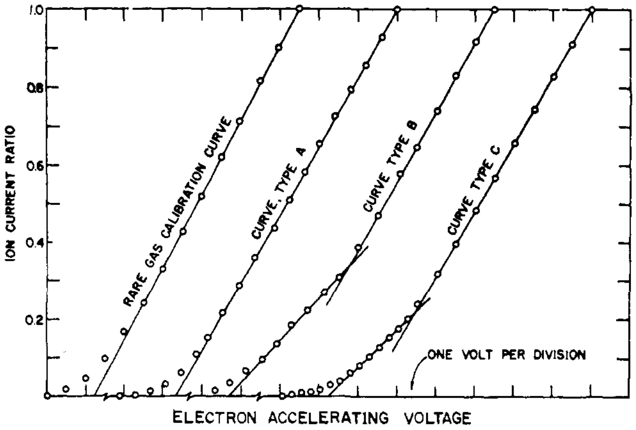

Figure 2. Comparison of normalized ionization efficiency curve shapes for rare gas, the amino acids, and fragments: type A observed for glycine and methionine parent ions, type B observed for all other parent ions, type C observed for all the fragment ions studied.

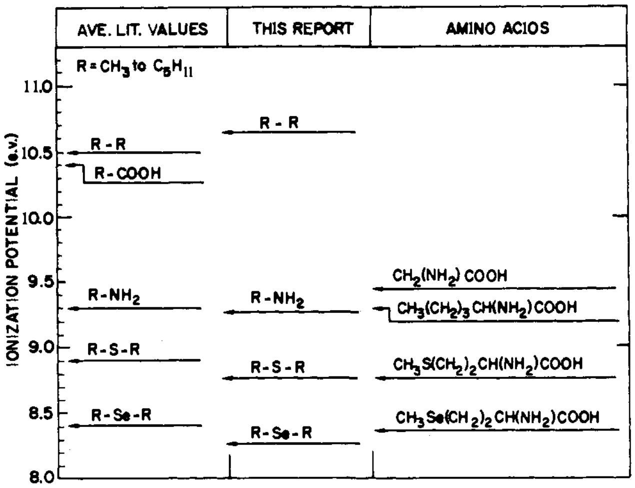

Figure 3. Energy diagram of ionization potentials. The R–Se–R is an interpolated value.

obtain ionization efficiency plots near threshold. The argon-krypton plots are shown in Figure 1. Other curves representative of the molecule ions and fragment ions from the amino acids are shown in Figure 2.

Table I. Difference in Ionization Potential (ΔIP) for Argon-Krypton Mixture *vs.* Data Treatment

Method	ΔIP, ev	Ref
Spectroscopic (std)	1.77	4
Vanishing current plots	2.01	11
Vanishing current (1 % level)	1.95	*a*
Vanishing current (direct)	1.80	11
Extrapolated difference	1.85	*b*
Ratio extrapolation	1.92	12

[a] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951). [b] J. W. Warren, *Nature*, **165**, 810 (1950).

Materials. The glycine, norleucine, and methionine were Calbiochem, grade A, further purified by vacuum sublimation at 170° prior to direct insertion into the ion chamber. The sample of selenomethionine was graciously supplied by Dr. A. L. Tappel of the University of California, Davis, and was used without further purification. All other samples were commercially supplied research grade materials (Aldrich Chemical Co. Inc.) and were used without additional purification.

Results and Discussions

Measured Ionization Potentials. A range of values have been published[4–7] for the measured ionization potentials of alkanes and monosubstituted alkanes. The average values for alkanes, aliphatic acids, amines, sulfides, and selenides are listed in Table II, column 2. The number of values taken from original references which were used to compute these averages is given in column 3. Although the ionization potential for a particular homologous group will vary slightly as a function of the degree of branching and the length of the hydrocarbon chain, these average values are a good indication of the relative energy requirements for ionization in each class of compounds. An energy diagram (Figure 3) clearly depicts the descending ionization energies: alkane $\geq$ aliphatic acid $\gg$ amine $>$ sulfide $>$ selenide.

The average literature value for butane, two alkyl sulfides, two alkylamines, and our own values (both ratio-extrapolation (RE) and vanishing-current (VC) results) for these same materials are also tabulated in Table II. These results agree generally with the average literature values so that comparison of our values with those of the literature seems legitimate. This comparison is graphically depicted in columns 1 and 2 of Figure 3. Our measured ionization potentials for this limited selection of compounds (butane and four monosubstituted alkanes) agrees within 0.2 ev with the average literature values for each class of compounds.

The most significant tabulation in Table II is the ionization potentials of the polysubstituted alkanes (the amino acids), glycine, norleucine, methionine, and selenomethionine. The vanishing-current values for these samples are recorded in column 3 of the energy diagram (Figure 3). Visual inspection of the entire energy diagram leads to the conclusion that the ionization of glycine and norleucine proceeds as if these molecules were simple aliphatic amines. There appears to be no measurable influence of the carboxyl group on the amount of energy necessary to effect ionization. Similarly, methionine and selenomethionine ionize independently of measurable effects from either or both the amino and carboxyl groups.

Table II. Ionization Potential of Alkanes and Substituted Alkanes

Sample	IP,[a] ev	No. of ref	Present report[b] RE method	Present report[b] VC method
C_nH_{2n+2} (n = 4–6)	10.5 ± 0.3	21	...	...
$CH_3(CH_2)_2CH_3$	10.7 ± 0.2	12	10.9 ± 0.3	10.71 ± 0.15
Aliphatic acids (C_2–C_4)	10.4 ± 0.1	8	...	...
$CH_3(CH_2)_2COOH$	10.2	1	...	...
Primary amines (C_4–C_5)	9.3 ± 0.2	9	9.5 ± 0.3	9.16 ± 0.15
$CH_3(CH_2)_3NH_2$	9.4 ± 0.2	3	9.5 ± 0.3	9.02 ± 0.10
$CH_3(CH_2)_2CH(NH_2)CH_3$	...	...	9.5 ± 0.2	9.31 ± 0.15
Sulfides (C_2–C_4)	8.9 ± 0.3[c]	7	8.8 ± 0.3	8.68 ± 0.10
$CH_3SC_2H_5$	9.0 ± 0.3[c]	2	8.8 ± 0.2	8.77 ± 0.10
$CH_3SC_3H_7$	9.1 ± 0.3[c]	2	8.8 ± 0.3	8.58 ± 0.10
Selenides	8.2 ± 0.2[d]	...	...	...
$CH_2(NH_2)COOH$	9.5[e]	1	9.6 ± 0.2	9.25 ± 0.10
$CH_3(CH_2)_3CH(NH_2)COOH$	9.5[e]	1	9.5 ± 0.1	9.09 ± 0.11
$CH_3S(CH_2)_2CH(NH_2)COOH$	9.5[e]	1	8.9 ± 0.1	8.63 ± 0.10
$CH_3Se(CH_2)_2CH(NH_2)COOH$	...	...	8.4 ± 0.1	8.29 ± 0.15

[a] Average values taken from ref 4 and 5 unless otherwise designated. [b] RE = ratio extrapolation; VC = vanishing current using direct observation as described in ref 11. [c] See ref 4, 5, and B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 1648 (1962). [d] Interpolated from literature values of S, Se, H_2Se, and $CH_3SCH_2CH_2CH_3$. [e] See ref 8 and discussion in the introduction.

In Figure 3, the energy necessary to ionize *individual* amino acids is compared with the average energy necessary to ionize *generally* related molecules. A more exact comparison is possible from results for molecules which have a close structural relationship to these amino acids. Ionization potentials of such molecules are tabulated as part of Table III and are shown graphically in the energy diagrams given in Figures 4 and 5. The structurally identical ethylamine–glycine pair is shown at the top of Figure 4. Similar though not identical structures exist for the 2-aminopentane–norleucine pair shown at the bottom. One immediately notes that the ionization potentials of each pair are the same within the estimated experimental accuracy limits of 0.2 ev.

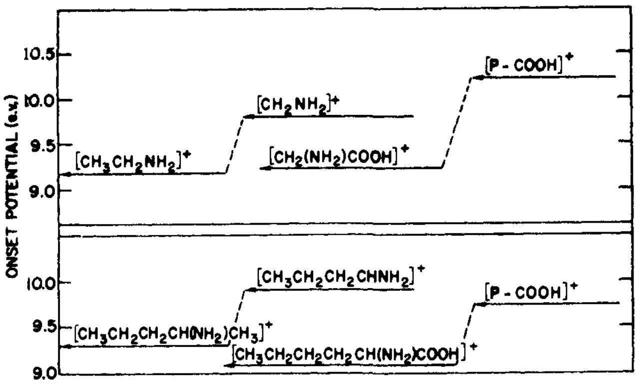

Figure 4. Ionization and fragment ion onset potentials of structurally identical substituted alkanes. The ionization potential of ethylamine and the appearance potential of the $[CH_2\text{–}NH_2]^+$ fragment ions are adjusted values taken from Collin (see footnote *d*, Table III).

A similar observation is made from Figure 5 where the methyl propyl sulfide–methionine and methyl propyl selenide–selenomethionine pairs are shown. It is legitimate to consider these pairs as structurally identical because the addition of two methylene groups to the sulfide and to the selenide should only slightly decrease their ionization potentials.

The accuracy limits of these results overshadow the possible significance of the small differences observed in the ionization potentials. Admittedly, these differences could be shown to be significant in future more accurate studies. However, from the present expected limits of accuracy for measurements on complex molecules, it can be concluded that the ionization potential of a polysubstituted alkane is the same as the potential of the structurally identical monosubstituted alkane which has the lowest value. The other substituents, provided they are separated by at least two carbon atoms, exert an unobservable effect upon the energy required to remove an electron from the molecular system. For convenience, this concept is termed "isolated ionization." If such a concept is correct, the ionization of substituted alkanes is more a property of the substituent united atom (where NH_2 and COOH are considered as a single atom) combined with the adjacent carbon atoms than of the molecule as a whole. In this respect, the charge resulting from ionization may be considered to be truly localized, as is often assumed in the original literature[13–15] or implied in

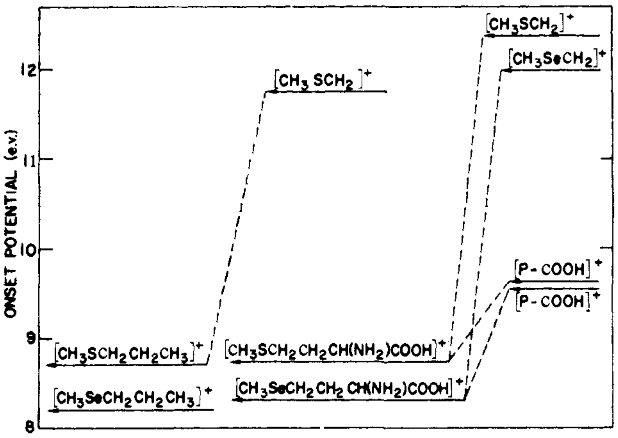

Figure 5. Ionization and fragment ion onset potentials of structurally identical substituted alkanes. The ionization potential of methyl propyl selenide is interpolated (see footnote *d*, Table II).

(13) A. G. Sharkey, J. L. Schultz, and R. A. Friedel, *Anal. Chem.*, **31**, 87 (1959).

(14) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(15) W. P. Chupka and J. Berkowitz, *J. Chem. Phys.*, **32**, 1546 (1960).

Table III. Ionization Potentials and Fragment Ion Onset Potentials

Sample	Fragment	Method RE	Method VC	Method LE[a]
Glycine	(Parent)$^+$	9.6 ± 0.2	9.25 ± 0.10	9.5 ± 0.4
	(P-COOH)$^+$	10.4 ± 0.3	10.23 ± 0.09	10.1 ± 0.4
Norleucine	(Parent)$^+$	9.5 ± 0.2	9.09 ± 0.11	9.5 ± 0.4[b]
	(P-COOH)$^+$	10.3 ± 0.2	9.76 ± 0.05	9.9 ± 0.4
Methionine	(Parent)$^+$	8.0 ± 0.1	8.63 ± 0.10	9.5 ± 0.4
	(P-COOH)$^+$	10.2 ± 0.2	9.68 ± 0.15	10.2 ± 0.4
	(CH_3SCH_2)$^+$	12.5 ± 0.2	12.43 ± 0.10	. . .
	(CH_3S^+)	13.0 ± 0.2	. . .	. . .
Selenomethionine	(Parent)$^+$	8.4 ± 0.2	8.29 ± 0.15	. . .
	(P-COOH)$^+$	10.1 ± 0.3	9.59 ± 0.20	. . .
	(CH_3SeCH_2)$^+$	12.8 ± 0.2	12.05 ± 0.14	. . .
Me-Pro-sulfide[c]	(Parent)$^+$	8.9 ± 0.3	8.58 ± 0.10	. . .
	(CH_3SCH_2)$^+$	11.6 ± 0.2	12.05 ± 0.14	. . .
	(CH_3S)$^+$	. . .	13.22 ± 0.21?	. . .
2-Aminopentane[d]	(Parent)$^+$	9.5 ± 0.2	9.31 ± 0.15	. . .
	(P-CH_3)$^+$	10.7 ± 0.3	9.92 ± 0.16	. . .
	(P-C_3H_7)$^+$	11.0 ± 0.2	10.43 ± 0.13	. . .

[a] LE = linear extrapolation; values taken from ref 8. A cylinder ion chamber described in ref 10 was used (see discussion in introduction). [b] These values are for isoleucine where the ionization potential should be less than 0.1v below norleucine. [c] See Hobrock and Kiser, footnote *c*, Table II, for a comparison with recent literature values for the same compound. [d] See J. Collin, *Bull. Soc. Chim. Belges*, **62**, 411 (1953); *Can. J. Chem.*, **37**, 1053 (1959), for literature values for this compound.

mass spectrometry books[16-18] when discussions and notations of ionization and fragmentation mechanisms are presented.

Calculated Ionization Potentials. In the calculation of ionization potentials by a united-atom approach,[2,3] an assumption is made which may be used to support this hypothesis of isolated ionization. As indicated in the introduction, interaction parameters were assumed to be zero for all but nearest neighbor united atoms. Nonetheless, the group orbital treatment is based on a concept which considers ionization as a true molecular property. The extent to which this ionization can be considered to be localized and in agreement with the experimental observations can be established by comparing the calculated potentials for several substituted alkanes. The calculated values based on the potential and interaction parameters listed in Table IV are recorded in Table V for some normal alkanes and several mono-, di-, and trisubstituted alkanes.

Table IV. Potential and Interaction Parameters[a]

Hydride	Potential parameter[b]	Interaction parameter[c]
CH_4	13.31	1.55
HCOOH	11.51	2.08
NH_3	10.52	1.46
H_2S	10.47	1.73

[a] Taken from ref 2. [b] The ionization potential of the hydride. [c] Indicative of the change in ionization potential caused by substitution of a saturated alkyl (usually methyl) for one of the hydrogens of the hydride.

Table V. Calculated Ionization Potentials of Substituted Alkanes[a]

Basic saturated structure	Identification no.	Calcd IP,[c] ev
C-C-C	0A	11.12
C-C-C-C-C-C-C	1A	10.43
C-C-C-C-C-(C)-C	2A	10.33
C-C-COOH	0C	10.70
C-C-N	0N	9.26
C-C-C-C-C-C-N	1N	9.23
C-C(C)-C-C-C-N	4N	9.23
C-C-C(C)-C-C-N	5N	9.22
C-C-C-C-C-N	8N	9.23
C-C(C)-C-C-N	11N	9.23
C-C-C(C)-C-N	12N	9.20
C-C-C-C-C(N)-C	2N	9.08
C-C-C-C(N)-C-C	3N	9.05
C-C(C)-C-C(N)-C	9N	9.08
C-C-C(N)-C-C	10N	9.06
C-C(C)-C(N)-C	13N	9.05
C-C-C-C-C(N)-COOH	2NC	8.99
C-C(C)-C-C-C(N)-COOH	6NC	8.98
C-C-C(C)-C(N)-COOH	7NC	8.95
C-C-C-C(N)-C-COOH	3NC	9.03
C-C-C(N)-C-C-COOH	18NC	9.05
C-C(N)-C-C-C-COOH	19NC	9.07
N-C-COOH	0NC	9.18
C-S-C-C-C[b]	14S	8.97
C-S-C-C	15S	8.98
C-S-C-C-C(C)-C	16S	8.97
C-S-C-C-C(C)-COOH	17SC	8.97
C-S-C-C-C(N)-COOH	2SNC	8.87
C-S-C-C(N)-C-COOH	3SNC	8.77
C-S-C(N)-C-C-COOH	10SNC	8.47
C-C-S-C-C(N)-COOH	20SNC	8.71
C-C-C-S-C(N)-COOH	21SNC	8.41

[a] All interaction and potential parameters are listed in Table IV. [b] The calculated values for the sulfur-substituted alkanes are lowered by ~0.3 ev if an interaction parameter of 1.99 is used; see Hobrock and Kiser, footnote *c*, Table II. [c] The discrepancies between the measured values given in Tables II and III and the calculated values listed here could be removed by suitable adjustments of the potential and interaction parameters. These adjustments are not relevant since the effects of carbon chain length, branching, and especially the addition of substituent groups are of more interest in this report than exact agreement of calculated and measured values.

Inspection of the calculated ionization potentials of sulfur or amino-substituted alkanes leads to the following observations. The ionization potentials of monosubstituted alkanes are relatively unaffected by carbon chain length and branching of the carbon chain pro-

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(16) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co. Inc., New York, N. Y., 1962.

(17) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964.

(18) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963.

vided this branching does not occur on the carbon which has the attached substituent. This is significantly different from the case of the *unsubstituted* alkanes. This conclusion applies to the sulfur and amino united atoms and probably is applicable to other substituents where the potential parameter of the hybride of the substituent is well below the potential parameter of methane.

A few specific comparisons in which the carbon skeletons are identical are interesting in the light of the experimental observations presented in the previous section. When a carboxyl substituent replaces a terminal methyl group (compare 0N with 0NC and 2N with 2NC), the calculated values agree within 0.1 ev. However, it should be noted that the agreement in both these cases, in which the carboxyl and amino groups are attached to the *same* carbon atom, would not be so favorable if methane and formic acid had different potential and interaction parameters. For example, the effect of these parameters cause a large reduction (~0.4 ev) in the calculated ionization potentials when the amino groups and the sulfur atom are attached to the *same* carbon atom as can be seen by comparing 21SNC and 10SNC with 2SNC, 3SNC, and 20SNC.

If the sulfur atom is separated from the other substituents by at least two carbon atoms (see 2SCN), the calculated ionization potential compares favorably with the calculated values for the disubstituted (17SC) and the monosubstituted (16S) alkanes having the same carbon skeleton.

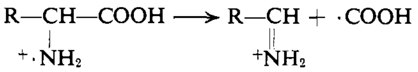
Calculated values for the alkyl selenides are not included in Table V because of a lack of experimental values from which proper interaction and potential parameters could be obtained. However, from a comparison of the ionization potentials of S and H_2S, Se and H_2Se, and an assumed interaction parameter equal to that used for sulfur, one can estimate that the calculated values for all selenium-substituted alkanes would be about 0.4 ev below the corresponding values for the structurally identical sulfur-substituted alkanes.

These comparisons of the calculated values for substituted alkanes indicate that long-range molecular interactions, though undoubtedly present, have a negligible effect upon ionization potentials. We therefore conclude that it is legitimate to consider the site of ionization to be "isolated" if one of the substituents has an ionization potential below that of the unsubstituted alkane. This isolated ionization concept, which follows from both experimental and calculated observations, suggests that the highest probability for removal of the electron during ionization is on or in the vicinity of the substituent. The term "localization of charge" and its notation as used or implied by others[13-18] in describing ionization and fragmentation mechanisms then suggests quite logically that for substituted alkanes the highest probability of locating the positive charge is in the vicinity of this substituent.[19]

Fragment Onset Potentials. The energy necessary to form selected fragment ions from the amino acids and monosubstituted alkanes (sulfides and amines) are also tabulated in Table III. These values and the literature values[20] for the ionization potential of methylamine and the onset potential for the $H_2C{-}NH_2^+$ fragment ion from methylamine are also shown on the energy diagrams in Figures 4 and 5. As was observed in the ionization-potential measurements, the onset potentials for formation of the fragment ions appear to be independent of the carboxyl and/or sulfur substituents. These observations are consistent with the hypothesis of isolated ionization.

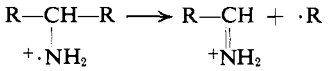
There is an interesting deduction which one can make from the observed onset potential for the $(P{-}COOH)^+$ fragments from both methionine and selenomethionine. These fragments from both substances appear at 9.6 to 9.7 ev. The $(P{-}COOH)^+$ fragment from norleucine, whose skeletal structure is identical with both these amino acids, appears at about the same energy, 9.8 ev. It is concluded from this observation that methionine and selenomethionine possess two sites at which an isolated ionization can occur, one in the vicinity of the sulfur or selenium atom and the other in the vicinity of the nitrogen atom. The $(P{-}COOH)^+$ fragment is formed by ionization at the nitrogen site and a subsequent simultaneous bond rupture and bond-forming process identical with that which occurs with norleucine.

The unimolecular decomposition of the parent ions of amines and amino acids by



$$R-\underset{\overset{|}{+\cdot NH_2}}{CH}-COOH \longrightarrow R-\underset{\overset{\|}{+NH_2}}{CH} + \cdot COOH \qquad (1)$$

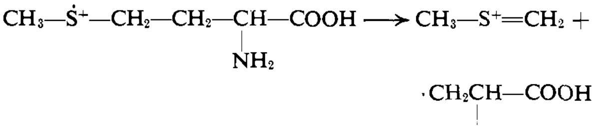
and



$$R-\underset{\overset{|}{+\cdot NH_2}}{CH}-R \longrightarrow R-\underset{\overset{\|}{+NH_2}}{CH} + \cdot R \qquad (2)$$

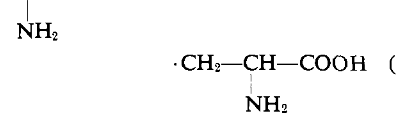
is supported by the appearance-potential measurements given here and in an earlier report.[8] However, the fragmentation of the alkyl sulfide,[17] methionine, and selenomethionine by

$$R-\dot{S}^+-CH_2-R \longrightarrow R-S^+{=}CH_2 + \cdot R \qquad (3)$$



$$CH_3-\dot{S}^+-CH_2-CH_2-\underset{\overset{|}{NH_2}}{CH}-COOH \longrightarrow CH_3-S^+{=}CH_2 + \cdot CH_2\underset{\overset{|}{NH_2}}{CH}-COOH \qquad (4)$$

and



$$CH_3-\dot{S}e^+-CH_2-CH_2-\underset{\overset{|}{NH_2}}{CH}-COOH \longrightarrow CH_3-Se^+{=}CH_2 + \cdot CH_2-\underset{\overset{|}{NH_2}}{CH}-COOH \qquad (5)$$

although intuitively legitimate are not supported by our appearance-potential measurements. From the data given in this report (Table III and Figure 5), part of which is substantiated by measurements from Hobrock and Kiser,[21] the proposed fragment ion, $(CH_3X^+{=}CH_2)$, appears at about 3.8 v above the

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[19] Comments by the referees on this manuscript questioned the possible implication that the authors wished to apply the "isolated ionization" concept to molecules other than substituted alkanes. At present, we merely state that the concept strictly applies only to the substituted alkanes described in this report. The authors do suspect from our incomplete studies using phosphorus, halogen, and oxygen substituents on alkanes, and these same substituents on other molecules such as alkenes, alkynes and aromatics, that the concept is universally applicable within the limits imposed by the discussion in this report.

[20] See footnote *d*, Table III.

[21] See footnote *c*, Table II.

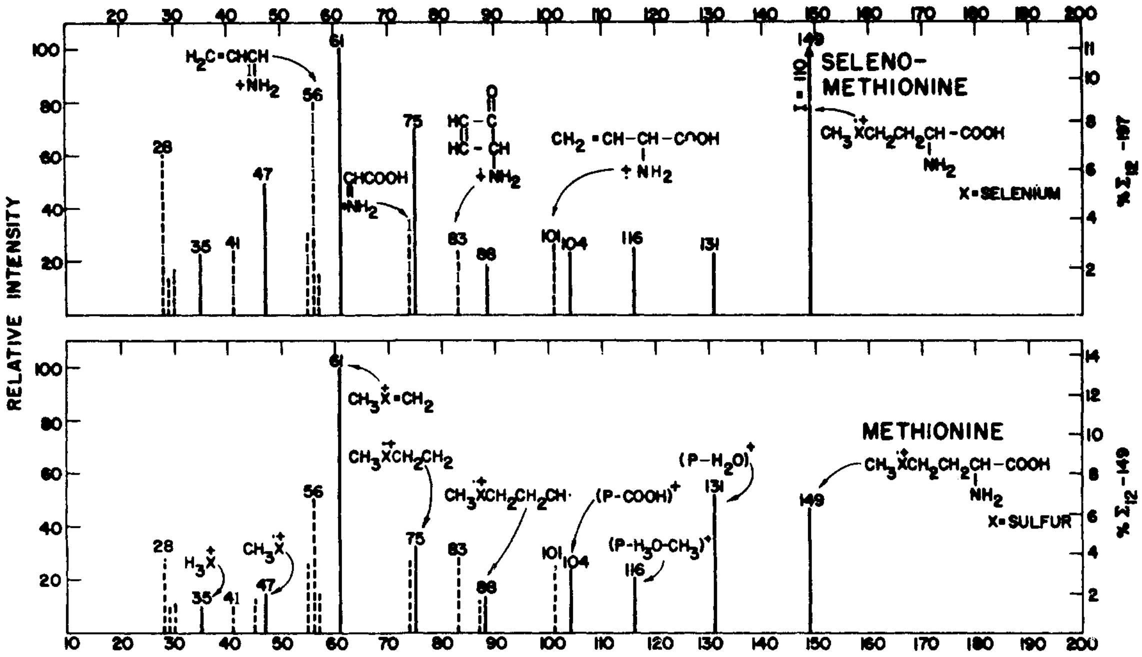

Figure 6. Mass spectra of methionine and selenomethionine corrected for isotope effects and the selenium–sulfur mass difference. The true mass of each fragment in the upper half of the figure is obtained by adding 48 to each peak indicated by a solid line.

ionization potential of the parent molecule ion. The bond-breaking and bond-forming processes as indicated in eq 3–5, which are similar to what appears to occur with the amines (eq 1 and 2), might be taking place. However, if the fragment ion is truly $RX^+{=}CH_2$, then considerable extra energy must be distributed in the form of large and unexpected excitations or possibly consumed in the formation of two instead of one uncharged fragment. It is also possible that the fragment ion may be actually the diradical $(R{-}X^+{-}CH_2\cdot)$. To completely resolve speculations such as these requires detailed studies with instrumentation which is not currently available. These observations of the appearance potential of fragments from the sulfur- or selenium-substituted alkanes do not seriously detract from the established value of using reasonable mechanisms such as those represented by eq 1–5 to illustrate unimolecular decomposition. Rather, this is an experimental observation which supports the generally accepted consensus that many ion-source reaction mechanisms cited in the literature in the form of two-dimensional structural formulas do not give a completely accurate description of the true unimolecular decomposition.

Fragmentation Probabilities. Line diagrams of the 70-ev mass spectra of methionine and selenomethionine are given in Figure 6. All isotope peaks have been summed so that each peak represents the entire contribution of the elemental composition. Note that those peaks from selenomethionine which include the selenium atom have been displaced 48 mass units (the Δm between ^{80}Se and ^{32}S) so that similarities and differences in the two spectra are readily evident from the resultant coincidence of the mass scale. Only the association between the intensities and the appearance potentials for the $(P{-}COOH)^+$ and "$CH_3X^+{=}CH_2$" fragments are discussed here.

The energy required to form the $(P{-}COOH)^+$ fragments from both amino acids is about 3.0 ev less than that necessary to form the "$CH_3X^+{=}CH_2$" fragments. Nevertheless, the frequency of formation of the sulfur- or selenium-containing fragments is nearly four times greater. The explanation for this observation could be related to the relative stabilities of the products of the two decompositions. A preferred alternative explanation is based on the isolated ionization concept developed above. If the energy necessary to effect ionization in the vicinity of the sulfur or selenium atom is less than that required to remove an electron from the vicinity of the nitrogen atom, ionization will occur more frequently at the sulfur or selenium position when the molecules interact with 70-ev electrons. The ionization probability for the lower energy process will be greatest, and subsequent fragmentation will depend upon the site of ionization.

Ease of removal of an electron is equated to the ability to accommodate the resultant positive charge so that the greatest probability for location of the charge in these cases is in the vicinity of the sulfur or selenium. Most of the molecules absorb additional energy from the 70-ev impacting electrons, and the statistical distribution of this energy causes appreciable bond ruptures. Since only the positive fragments resulting from these bond ruptures are observed, the sulfur or selenium fragments occur with a much higher frequency than the $(P{-}COOH)^+$ fragments, simply because the probability of the charge being localized on the sulfur or selenium, compared to the amino substituent, is much higher.

It is probably not correct to correlate the intensities of the fragment currents produced by 70-ev electrons with those produced by electrons whose energy is near the ionization threshold. For example, the breaks in the ionization efficiency curves for the fragment ions shown in Figure 2 indicate that the fragmentation and possibly even the ionization mechanisms are energetically different and more complex when 70-ev electrons are used compared to what occurs within a few volts of onset. From the present quality of our data, no consistent correlations can be made between the observed intensities of the various fragment currents and the breaks which are observed in the ionization efficiency curves.

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Energy and Entropy of Activation of Propagation by the Free Polystyryl Anions and Their Ion Pairs. The Phenomenon of "Negative" Activation Energy.

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Abstract: The anionic polymerization of sodium and cesium salts of living polystyrene was investigated in tetrahydrofuran between -70 and $+25°$. Under these conditions both salts are partially dissociated into free ions, and the respective dissociation constants, K_{dis}, were determined from conductance studies of their solutions. For the sodium salt, K_{dis} increases from 1.5×10^{-7} at 25° to 300×10^{-7} M at $-70°$, the heat of dissociation being -8 kcal/mole in the interval -30 to $+25°$ and about -6 kcal/mole at $-70°$. The cesium salt is less dissociated, K_{dis} being 0.047×10^{-7} at 25° and 0.1×10^{-7} M at $-60°$; thus the respective ΔH is -1.8 kcal/mole only. The kinetic data showed that the free $\sim\!\!\sim\mathrm{S}^-$ ions and the respective ion pairs participate in the propagation. Studies of either salt led to concordant results for the propagation constant, k_-, of the free ions, *viz.*, $k_- = 65{,}000$ at 25° and about 1000 M^{-1} sec^{-1} at $-70°$. Thus, $E_- \approx 6$ kcal/mole and $A_- \approx 10^9$ M^{-1} sec^{-1}. The cesium ion pair behaves conventionally; its propagation rate constant, $k_{\pm.\mathrm{Cs}}$, decreases from 25 at 25° to about 1 M^{-1} sec^{-1} at $-60°$. However, $k_{\pm}$ for the sodium ion pair *increases* from 80 at 25° to about 270 M^{-1} sec^{-1} at $-60°$. The reasons for this negative "activation energy" are fully discussed. The $\sim\!\!\sim\mathrm{S}^-,\mathrm{Na}^+$ might exist in two forms, a virtually unreactive contact ion pair and a highly reactive solvent-separated ion pair. The equilibrium favors the latter at lower temperatures, and this may account for the results. However, such an interpretation is not unique, and an alternative hypothesis has been also proposed.

Propagation of anionic polymerization in ethereal solvents involves free ions and ion pairs. For example, in tetrahydrofuran (THF) the free polystyrene ion, $\sim\!\!\sim\mathrm{S}^-$, grows with a rate constant $k_- = 65{,}000$ M^{-1} sec^{-1} at 25°, whereas the respective rate constants of the ion pairs seem to be 160, 80, and 25 M^{-1} sec^{-1} for the Li^+, Na^+, and Cs^+ salts.[1]

We have now determined the activation energy and the entropy of activation for the propagation of the free $\sim\!\!\sim\mathrm{S}^-$ ion and of its sodium and cesium salts (ion pairs) in THF. This was accomplished by investigating the kinetics of the over-all propagation over a wide temperature range (-70 to $+25°$) and by determining the dissociation constants of $\sim\!\!\sim\mathrm{S}^-,\mathrm{Na}^+$ and $\sim\!\!\sim\mathrm{S}^-,\mathrm{Cs}^+$ salts in THF.

Experimental Section

Purification of the monomer and the solvent and details of preparation of the living polystyrenes were previously reported.[1b,2] Benzylsodium was used for the preparation of "one-living-end" polystyrene. The initiator was synthesized on a high-vacuum line by treating dibenzylmercury (1 g dissolved in 70 cc of THF) with a sodium mirror at $-20°$. The reaction was completed in about 4 hr, and the resulting brownish red solution of $\mathrm{PhCH_2^-,Na^+}$ was filtered from the excess of the alkali metal and then treated with 1.9 g (about sevenfold excess) of α-methylstyrene. A direct addition of styrene was found unsatisfactory, since the propagation is then faster than the initiation.[3] The propagation of α-methylstyrene is slow and reversible, and hence the conversion of $\mathrm{PhCH_2^-,Na^+}$ into $\mathrm{PhCH_2CH_2C(Ph)(CH_3)^-,Na^+}$ is quantitative. The addition of styrene to the latter species is faster than the homopropagation of living polystyrene,[4] and therefore its conversion into $\sim\!\!\sim\mathrm{S}^-,\mathrm{Na}^+$ is quantitative.

Dropwise addition of 4 g of styrene dissolved in ~10 cc of THF (distilled from benzylsodium) to the vigorously stirred solution of $\mathrm{PhCH_2CH_2C(Ph)(CH_3)^-,Na^+}$ kept at $-50°$ was followed by a vacuum distillation of an additional 1 g of styrene into the reacting mixture. The final yield of living polystyrene, based on the dibenzylmercury, was about 75%; the average degree of polymerization (DP) of the resulting "one-living-end" polystyrene was calculated to be about 12.

The one-ended polystyrylcesium salt was prepared from cumylcesium.[1b] The cumyl ether used in the preparation of cumylcesium must be freshly prepared, because it slowly decomposes into α-methylstyrene and methanol even if kept in sealed ampoules under vacuum in a freezer. The presence of α-methylstyrene leads to formation of the undesirable two-ended polystyrylcesium.

Recrystallized $\mathrm{Na^+,BPh_4^-}$ was dissolved in rigorously dried THF, and the required amounts were introduced into ampoules equipped with breakseals. The solvent was then slowly evaporated on a high-vacuum line, the residue was dried by pumping, and after a few hours the ampoules were sealed off. An appropriate ampoule was sealed to the reaction vessel whenever needed.

Studies of Conductance of the Living Polystyrenes. A detailed description of the technique used in the conductance studies is given elsewhere.[1,5] The conductance was measured for a series of con-

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