difference between the two transition states is substantially lower than that between I and the first transition state for ionization. On the other hand, a single-maximum potential energy diagram is sufficient for nonpolar solvents.

Conclusion

The complementary evidences gained from this spectral, kinetic, and equilibrium study lead to the conclusions that (a) the colored transients from indolinospiropyrans are zwitterionic; (b) these colored transients exist in solution as an equilibrium distribution distribution of steroisomers; (c) the dominant isomer in nonpolar solvents is a planar *trans*-monomeric species, while that in polar and hydroxylic media is a dimeric and/or associated species. It is shown that the effect of solvent on the visible absorption spectra of the transients from indolinospiropyrans parallels that for the ionic cyanine dyes.[20] This with the kinetic and equilibrium data presented indicate that contributions from quinoid species are probably minimal rather than dominant, as was previously thought[17] from spectral comparisons with the nonionic merocyanines.

An intriguing, but as yet unexplained feature of this work is the extremes of spectral and kinetic behavior exhibited by the indolinospiropyrans and the simple pyran and benzopyran.[46] In the latter cases the transient photoproduct appears to be a molecular species. In contrast, the action of the indolino nucleus in conferring definite zwitterionic character to the transient photoproduct from spiropyrans is dramatic. This apparent ability of the indolino substituent to stabilize ionic structures is of continuing research interest in this laboratory.

Acknowledgments. The assistance of Miss Anita VanLaeken in preparation of the compounds studied and many helpful discussions with Dr. Alan Monahan throughout the course of this work are acknowledged with sincere gratitude. It is a pleasure to thank Jeraldine Allen, to whom fell the task of manuscript preparation.

The Fragmentation of Aliphatic Sulfur Compounds by Electron Impact

B. G. Keyes and A. G. Harrison

Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Canada. *Received March 14, 1968*

Abstract: The energetics of formation of the molecule ion and sulfur-containing fragment ions have been examined for a number of simple aliphatic mercaptans and sulfides. The following fragment ion heats of formation have been obtained (all in kcal/mole): CH_3S^+, 214; CH_2SH^+, 220; $CH_3SCH_2^+$, 205; $C_2H_5S^+$, 202; CH_3CHSH^+, 197. The mass spectra of labeled sulfides and mercaptans have been compared with the analogous oxygen compounds. The sulfur compounds show increased intensities for the molecule ion and fragment ions originating by cleavage of the bond to the heteroatom, with a decreased abundance of ions originating by α cleavage. This is shown to be due primarily to the decreased stability of the ions formed by α cleavage in the sulfur compounds and not to the increased stability of RS^+ ions.

The mass spectra of simple aliphatic mercaptans and sulfides, when compared with the spectra of the corresponding alcohols and ethers, show significantly greater abundances of both the molecule ion and fragment ions formed by cleavage of bonds to the heteroatom, coupled with a reduced abundance of ions resulting from α cleavage with charge retention on the heteroatomic fragment.[1] The reasons for these differences are not clear; however, in terms of the quasi-equilibrium theory of mass spectra, they are most readily explained on the basis of the relative activation energies of the fragmentation reactions involved. The energetics of the fragmentation reactions have been reasonably well established for simple alcohols and ethers.[2,3]

Although several groups[4-8] have reported appearance potentials of fragment ions from organic sulfur compounds, no systematic investigation of the energetics of formation of the various isomeric ions has been made, with the result that the energetics of the fragmentation reactions in sulfur compounds are not clearly established. The present work reports such a detailed study for ions of empirical formula CH_3S^+ and $C_2H_5S^+$. During this study we have used extensive deuterium labeling to distinguish ionic structures which would otherwise have the same mass-to-charge ratio. The spectra of these labeled sulfur compounds, when compared to the spectra of the corresponding labeled alco-

---

(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967.

(2) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).

(3) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964).

(4) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).

(5) T. F. Palmer and F. P. Lossing, *ibid.*, **84**, 4661 (1962).

(6) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 1648 (1962).

(7) B. G. Hobrock and R. W. Kiser, *ibid.*, **67**, 1283 (1963).

(8) B. G. Gowenlock, J. Kay, and J. R. Majer, *Trans. Faraday Soc.*, **59**, 2463 (1963).

hols and ethers, serve to emphasize the differences observed in the mass spectra.

Experimental Section

All mass spectra and appearance potentials were measured using an AEI MS-2 mass spectrometer modified as described previously.[9] Mass spectra were obtained at 75-V electron energy with a repeller field of 3–5 V/cm. The ionization efficiency curves for the ion of interest and the standard, usually krypton, were plotted in the semilogarithmic manner.[10] For molecular ions these curves were parallel and the voltage difference could be determined directly. For fragment ions the curves frequently were nonparallel, and in these cases the threshold voltage was evaluated by extrapolation of the voltage difference curve to zero ion current. The error limits quoted represent the average deviation of three or more determinations of the onset potential.

All unlabeled sulfur compounds were commercially available samples and showed no detectable impurities in their mass spectra. Methyl-d_3 mercaptan, ethyl-d_5 mercaptan, and methyl-d_3 methyl sulfide were obtained from Merck Sharp and Dohme, Montreal. Methyl-d_3 ethyl sulfide was prepared by the reaction of ethyl mercaptan with methyl-d_3 bromide (Merck Sharp and Dohme) in alcoholic KOH, while ethyl-d_5 ethyl sulfide was prepared in the same manner from ethyl mercaptan and ethyl-d_5 bromide (Merck Sharp and Dohme). Final purification in both cases was by gas chromatography. The isotopic purity of each deuterated compound was determined at low voltages and found to be better than 97% for all compounds except ethyl-d_5 ethyl sulfide which was approximately 95% d_5. The partial mass spectra have been corrected for the isotopic impurities as well as for C^{13} and the heavier sulfur isotopes.

Results and Discussion

Comparison of Fragmentation of Sulfur and Oxygen Compounds. The intensities (% total ionization) of the major sulfur-containing ions in the mass spectra of CD_3SH, C_2D_5SH, CH_3SCD_3, and $C_2H_5SCD_3$ are compared in Table I with the intensities of the corresponding ions in the mass spectra of the labeled oxygen analogs. With the exception of the spectrum of C_2D_5OH,[11] all spectra were run on the same instrument under very similar conditions. The comparison clearly shows that in all cases the molecule ion is a greater per cent of the total ionization for the sulfur compounds than for the oxygen compounds. Similarly, the RS^+ ions are of considerably greater intensity than the corresponding RO^+ ions as shown, for example, by the large intensities for the CD_3S^+ ion in the mass spectra of CD_3SH and CD_3SCH_3 compared to the intensities for CD_3O^+ in the spectra of CD_3OH and CD_3OCH_3. The intensities of the ions formed by α cleavage are considerably lower in the mercaptans and sulfides than in the oxygen compounds as shown by the comparison of the intensities of CD_2XH^+ in the spectra of CD_3XH and C_2D_5XH and the intensities of $CD_2XCH_2^+$ in the spectra of $CD_3XC_2H_5$.

Table I. Comparison of Fragmentation of Sulfur- and Oxygen-Containing Molecules

Ion	Intensity (% total ionization) X ≡ S	X ≡ O
CD_3XH^+	34.3	30.9
CD_3X^+	12.0	<2.4
CD_2XH^+	26.0	42.1
$C_2D_5XH^+$	23.2	6.4
$C_2D_5X^+$	0.6	0
$C_2D_4XH^+$	1.57	14.7
CD_2XH^+	14.7	41.6
$CH_3XCD_3^+$	24.1	17.7
$CD_3XCH_2^+$	4.71	25.7
$CH_3XCD_2^+$	2.73	15.0
CD_3X^+	9.71	0.64
CH_3X^+	14.1	1.05
$C_2H_5XCD_3^+$	21.0	10.8
$CD_3XCHCH_3^+$	0.92	4.67
$C_2H_5X^+$	5.40	<0.2
$CD_3XCH_2^+$	21.8	39.8
CD_3X^+	3.17	0.5
CD_2XH^+	4.62	4.64

A further significant difference between the sulfur and oxygen compounds is the relatively larger abundance of alkyl ions found in the mass spectra of the sulfur compounds. The origin of the alkyl ions in the spectra of ethers, particularly, appear to be varied and complex. In the present paper we will concern ourselves only with the relative energetics of formation of the heteroatomic fragment ions.

Energetics of Ion Formation in Mercaptans and Sulfides

Molecule Ions. The ionization potentials, measured in the present work, for a number of mercaptans and sulfides are compared with previous values in Table II. The agreement of the present results with previous measurements,[6–8] particularly those obtained by photoionization,[12] provides confirmation that the electron energy scale has been correctly established. The ionic heats of formation for the molecule ions, which are required for subsequent calculations (Tables VI and VII), are tabulated in the final column of Table II. The ancillary thermochemical data needed for these calculations and all further calculations are summarized in the Appendix.

Table II. Molecular Ionization Potentials

Molecule	Ionization potential, eV: This work	Electron impact[a]	Photoionization[12]	ΔH_f(ion), kcal/mole
$C_2H_5SC_2D_5$	8.55 ± 0.1	8.6,[8] 8.49[7]	8.43	177
$C_2H_5SCH_3$	8.54 ± 0.1	8.70[6]	8.55	183
CH_3SCH_3	8.71 ± 0.1	9.0,[8] 8.7[6]	8.69	192
CD_3SCH_3	8.72 ± 0.1	8.7[8]		192
C_2H_5SH	9.31 ± 0.1		9.29	204
CD_3SH	9.54 ± 0.1		9.44	215

[a] With exception of the value for CD_3SCH_3, all literature values are for the unlabeled molecule.

CH_3SH^+ and $CH_3SH_2^+$ from Methyl Alkyl Sulfides. The CH_3SH^+ and $CH_3SH_2^+$ ions are significant rearrangement ions in the spectra of CH_3SR where R contains at least two carbon atoms. The fragmentation reactions presumably are

$$CH_3SR^+ \longrightarrow CH_3SH^+ + (R\text{-}H) \qquad (1)$$

$$\longrightarrow CH_3SH_2^+ + (R\text{-}2H) \qquad (2)$$

Table III summarizes the data obtained in the present work for these two ions.

---

[9] T. W. Shannon, F. Meyer, and A. G. Harrison, *Can. J. Chem.*, **43**, 159 (1965).

[10] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

[11] L. W. Sieck, F. P. Abramson, and J. H. Futrell, *ibid.*, **45**, 2859 (1966).

[12] K. Watanabe, T. Nakayama, and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," University of Hawaii, Dec 1959.

Table III. Energetics of Formation of CH_3SH^+ and $CH_3SH_2^+$ Ions

Ion	Source	Appearance potential, eV		Neutral fragments	ΔH_f (ion), kcal/mole
		This work (±0.1)	Ref 6		
CH_3SH^+	$C_2H_5SCH_3$	10.43	11.8	C_2H_4	214
CD_3SH^+	$C_2H_5SCD_3$	10.48		C_2H_4	215
CH_3SH^+	n-$C_3H_7SCH_3$	10.45	11.3	C_3H_6	217
$CH_3SH_2^+$	$CH_3SC_2H_5$	10.7 ± 0.3	12.0	C_2H_3	167
$CH_3SH_2^+$	n-$C_3H_7SCH_3$	10.23	11.0	c-C_3H_5	163

Table IV. Energetics of Formation of CH_3S^+ and CH_2SH^+ Ions

Ion	Source	Appearance potential, eV		Neutral fragments	ΔH_f(ion), kcal/mole
		This work (±0.1 eV)	Lit.		
CH_3S^+	CH_3SCH_3	11.08	11.24,[5] 11.7,[7] 11.3,[8] 11.38[4]	CH_3	215
CD_3S^+	CD_3SH	11.76		H	214
CD_3S^+	$CD_3SC_2H_5$	12.69	14.7[6 a]	$C_2H_4 + H$ $C_2H_3 + H_2$	214 214
CH_2SH^+	C_2H_5SH	11.41		CH_3	220
CH_2SH^+	$C_2H_5SC_2H_5$	12.31	12.75,[8] 13.5[7]	$CH_3 + C_2H_4$	219
CD_2SH^+	CD_3SH	12.01		D	219

[a] Appearance potential of *m/e* 47 from unlabeled sulfide.

Our appearance potentials for CH_3SH^+ from methyl ethyl sulfide and methyl *n*-propyl sulfide are considerably lower than those reported previously.[6] However, the logical assumption that the fragmentation occurs by reaction 1 with ethylene and propylene, respectively, as the neutral fragments, leads to calculated values for $\Delta H_f(CH_3SH^+)$ in good agreement with that obtained from the direct ionization of methyl mercaptan (Table II). This agreement provides support for the present measurements.

The appearance potentials of the $CH_3SH_2^+$ ion from $CH_3SC_2H_5$ and $CH_3SC_3H_7$ were measured with the results summarized in Table III. Assuming C_2H_3 as the neutral fragment when R = ethyl, we calculate $\Delta H_f(CH_3SH_2^+) = 167$ kcal/mole. The fragmentation of methyl *n*-propyl sulfide presumably leads to formation of a C_3H_5 radical which may have either the allyl or cyclopropyl structure. Assumption of the allyl structure leads to $\Delta H_f(CH_3SH_2^+) = 186$ kcal/mole, while assumption of the cyclopropyl structure leads to $\Delta H_f(CH_3SH_2^+) = 163$ kcal/mole, in agreement with the value derived from methyl ethyl sulfide. It appears probable that the neutral C_3H_5 has the cyclopropyl structure. The cyclopropyl structure for the neutral has also been postulated[3,13] in the similar rearrangement of *n*-propyl and isopropyl esters.

An upper limit to $\Delta H_f(CH_3SH_2^+)$ can be derived from the observation[14] that the ion-molecule reaction

$$CH_3SH^+ + CH_3SH \longrightarrow CH_3SH_2^+ + CH_3S \qquad (3)$$

occurs and must therefore be thermoneutral or exothermic. This leads to an upper limit $\Delta H_f(CH_3SH_2^+) \leq 179$ kcal/mole. The experimental value of 165 ± 5 kcal/mole therefore does not appear unreasonable and leads to a calculated proton affinity of gaseous methyl mercaptan of 195 ± 5 kcal/mole.

Sulfur-Containing Ions of *m/e* 47. Two possible structures for sulfur-containing ions of *m/e* 47 are CH_3S^+ and CH_2SH^+. The former ion should result from simple fragmentation of methyl sulfides, while the latter should be obtained by α cleavage in *n*-alkyl mercaptans. The mass spectrum of CD_3SH (Table I) shows that both ions are obtained in the fragmentation of methyl mercaptan.

The appearance potential of CH_3S^+ from CH_3SCH_3 was found in the present work to be 11.08 eV. This is slightly lower than three previously reported measurements of 11.24, 11.3, and 11.38 eV and considerably lower than one reported value of 11.7 eV. Our appearance potential leads to $\Delta H_f(CH_3S^+) = 215$ kcal/mole in excellent agreement (Table IV) with $\Delta H_f(CD_3S^+) = 214$ kcal/mole derived from the appearance potential of CD_3S^+ from CD_3SH. The appearance potential of CD_3S^+ from $CD_3SC_2H_5$ was also measured and found to be 12.69 eV, considerably lower than the value of 14.7 eV reported[6] for *m/e* 47 from the unlabeled molecule. The lower value leads to $\Delta H_f(CD_3S^+) = 214$ kcal/mole only if we assume $C_2H_4 + H$ (or $C_2H_3 + H_2$) rather than C_2H_5, as the neutral fragments. The results support an average value $\Delta H_f(CH_3S^+) = 214 \pm 3$ kcal/mole.

The appearance potential of CH_2SH^+ was measured from C_2H_5SH and $C_2H_5SC_2H_5$, and, as shown in Table IV, both lead to ionic heats of formation, 220 and 219 kcal/mole, respectively, in good agreement. The neutral fragments in the case of $C_2H_5SC_2H_5$ indicate the fragmentation

$$C_2H_5SC_2H_5^+ \longrightarrow CH_3 + C_2H_5SCH_2^+ \longrightarrow C_2H_4 + HSCH_2^+ \qquad (4)$$

This route is supported by a metastable peak at *m/e* 29.5 corresponding to the second step of the above sequence and by the observation that the ion was found as CD_2SH^+ and CH_2SD^+ in the spectrum of $C_2H_5SC_2D_5$.

The appearance potential of CD_2SH^+ from CD_3SH leads to $\Delta H_f(CD_2SH^+) = 219$ kcal/mole, in excellent agreement with the values obtained for the CH_2SH^+ ion. The average value, 219 ± 3 kcal/mole, is not significantly greater than $\Delta H_f(CH_3S^+) = 214 \pm 3$ kcal/mole. However, observations in the same experiment of the CD_3S^+ and CD_2SH^+ ion currents from CD_3SH left little doubt that the appearance potential (and therefore heat of formation) of CD_2SH^+ was slightly higher than that of CD_3S^+.

Sulfur-Containing Ions of *m/e* 61. In the absence of rearrangement three likely structures for ions of *m/e*

---

(13) A. G. Harrison and E. G. Jones, *Can. J. Chem.*, **43**, 960 (1965).

(14) G. P. Nagy, J. C. J. Thynne, and A. G. Harrison, unpublished results.

61 are $C_2H_5S^+$, $CH_3SCH_2^+$, and CH_3CHSH^+. A further, less probable, structure is $HSCH_2CH_2^+$.

One would expect the $CH_3SCH_2^+$ ion to be formed by simple fragmentation of methyl alkyl sulfides according to

$$CH_3SCH_2R^+ \longrightarrow CH_3SCH_2^+ + R \qquad (5)$$

Thus the appearance potential (AP) of the ion with the nominal structure $CH_3SCH_2^+$ was measured from dimethyl sulfide (R = H) and methyl *n*-propyl sulfide (R = C_2H_5). For methyl ethyl sulfide (R = CH_3), the isomeric $C_2H_5S^+$ ion is also formed and in this case AP($CD_3SCH_2^+$) from $CD_3SC_2H_5$ was measured. The results are summarized in Table V. All appearance potentials lead to ionic heats of formation in good agreement and an average value $\Delta H_f(CH_3SCH_2^+)$ = 205 ± 3 kcal/mole.

Table V. Energetics of Formation of $CH_3SCH_2^+$ and $C_2H_5S^+$ Ions

Ion	Source	Appearance potential, eV This work (±0.1 eV)	Lit.	Neutral fragments	ΔH_f (ion), kcal/mole
$CH_3SCH_2^+$	CH_3SCH_3	11.5$_0$	11.8[7]	H	204
$CH_3SCH_2^+$	*n*-$C_3H_7SCH_3$	10.9$_7$	11.9[6]	C_2H_5	208
$CD_3SCH_2^+$	$CD_3SC_2H_5$	10.8$_4$	*a*	CH_3	204
$C_2H_5S^+$	$CD_3SC_2H_5$	10.7$_5$	*a*	CD_3	202
$C_2H_5S^+$	$C_2H_5SC_2D_5$	10.7$_2$	*b*	C_2D_5	202

[a] Reference 6 has reported AP(*m*/*e* 61) = 11.8 eV from C_2H_5-SCH_5. Our measurement gave 10.7$_4$ eV in agreement with AP-($C_2H_5S^+$) from $C_2H_5SCD_3$. [b] Reference 4 has reported AP(*m*/*e* 61) = 11.15 eV from $C_2H_5SC_2H_5$.

The $C_2H_5S^+$ ion should be formed from ethyl sulfides by the simple cleavage

$$C_2H_5SR^+ \longrightarrow C_2H_5S^+ + R \qquad (6)$$

In the present work AP($C_2H_5S^+$) was measured from $C_2H_5SCD_3$ and $C_2H_5SC_2D_5$. The deuterium labeling is necessary in both cases to distinguish between the $C_2H_5S^+$ ion and isomeric ions of the same mass in the unlabeled molecule. The two appearance potentials both lead to $\Delta H_f(C_2H_5S^+)$ = 202 kcal/mole.

To establish the heat of formation of the ion nominally of structure CH_3CHSH^+, the appearance potential of *m*/*e* 61 from isopropyl mercaptan was measured. The experimental appearance potential, 10.74 ± 0.1 eV, leads to $\Delta H_f(CH_3CHSH^+)$ = 197 ± 3 kcal/mole. It was hoped to provide support for this determination by measuring AP($C_2D_4SH^+$) from C_2D_5SH since, by analogy with ethyl alcohol, one might expect loss of the α-deuterium only. The appearance potential, 11.85 ± 0.1 eV, leads to $\Delta H_f(C_2D_4SH^+)$ = 210 kcal/mole. The discrepancy of 13 kcal/mole between the two heats of formation is beyond the limits of experimental error, and it may be that the ion derived from ethyl-d_5 mercaptan has the structure $HSCD_2CD_2^+$. We have taken the lower value, 197 ± 3 kcal/mole, as the best value for $\Delta H_f(CHSH^+)$.

In summary the heats of formation (kcal/mole) of the three major ions at *m*/*e* 61 have been found to be $CH_3SCH_2^+$, 205; $C_2H_5S^+$, 202; CH_3CHSH^+, 197. Within reasonable experimental error these values cannot be distinguished from each other and, therefore, it cannot be stated with certainty that the ions do, in fact, have the structure predicted from the structure of the neutral molecule. On the other hand, the identity of heats of formation does not prove that the ions all have the same structure. Whether or not the ionic heats of formation actually refer to the indicated structures is of secondary importance in any attempt to understand the energetics basis of the fragmentation of the respective molecule ions. The deuterium labeling clearly shows that hydrogen scrambling between the various parts of the molecule does not occur prior to the formation of fragment ions either by cleavage of the α bond or the bond to the heteroatom. Thus the measured onset potentials are (within the experimental limits of error) a true measure of the minimum energy required to produce fragment ions by either of these possible cleavages, regardless of the structure of the fragment ions produced.

Heats of Formation of C_2H_5S and CH_3S Radicals. From measurements of the appearance potentials of $C_2H_5S^+$ from $C_2H_5SC_2H_5$ and $C_2H_5SSC_2H_5$, Franklin and Lumpkin[4] derived $\Delta H_f(C_2H_5S)$ = 25 kcal/mole. This value has been recalculated[15] to be 28 ± 3 kcal/mole using more recent data on $\Delta H_f(C_2H_5SSC_2H_5)$. Franklin and Lumpkin's AP($C_2H_5S^+$) = 11.15 eV from $C_2H_5SC_2H_5$ leads to $\Delta H_f(C_2H_5S^+)$ = 213 kcal/mole, considerably higher than the average value determined in this work. Combining our $\Delta H_f(C_2H_5S^+)$ = 202 kcal/mole with their AP($C_2H_5S^+$) = 11.18 eV from $C_2H_5SSC_2H_5$ leads to $\Delta H_f(C_2H_5S)$ = 38 kcal/mole, a value which appears impossibly high. We have therefore redetermined the appearance potential of $C_2H_5S^+$ from the disulfide and obtained the much lower value of 10.47 eV. From this value and $\Delta H_f(C_2H_5S^+)$ = 202 kcal/mole, we calculate $\Delta H_f(C_2H_5S)$ = 22 ± 4 kcal/mole, in reasonable agreement with the value of 25 ± 5 kcal/mole estimated by Mackle.[15]

The heat of formation of CH_3S has been calculated[15] to be 36 kcal/mole from the data of Franklin and Lumpkin[4] for the appearance potential of CH_3S^+ from dimethyl sulfide and dimethyl disulfide. Their data correspond to $\Delta H_f(CH_3S^+)$ = 221 kcal/mole. Use of our lower value, $\Delta H_f(CH_3S^+)$ = 214 kcal/mole, would lead to $\Delta H_f(CH_3S)$ = 42 kcal/mole when combined with Franklin and Lumpkin's AP(CH_3S^+) = 11.38 eV from $(CH_3S)_2$ and $\Delta H_f(CH_3S)$ = 36 kcal/mole when combined with Palmer and Lossing's[5] value of AP(CH_3S^+) = 11.12 eV. Both values are considerably higher than the estimate[15] of 30.5 ± 5 kcal/mole from thermal data. Our remeasurement of AP(CH_3S^+) from $(CH_3S)_2$ gave 11.34 eV in good agreement with previous values. We are unable to explain why the indirect method gives satisfactory results for the C_2H_5S radical but not for the CH_3S radical.

Palmer and Lossing[5] derived $\Delta H_f(CH_3S) \leq 31.8$ kcal/mole from the directly measured IP(CH_3S) $\leq$ 8.06 eV and $\Delta H_f(CH_3S^+)$ = 217.7 kcal/mole derived from their appearance potential of CH_3S^+ from dimethyl sulfide. Our value, $\Delta H_f(CH_3S^+)$ = 214 kcal/mole, when combined with the radical ionization potential yields $\Delta H_f(CH_3S) \leq 28$ kcal/mole, a value which is still in good agreement with the thermal estimate of 30.5 ± 5 kcal/mole.

---

(15) H. Mackle and R. G. Mayrick, *Trans. Faraday Soc.*, **58**, 33 (1962); H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

Comparison of Energetics of Ion Formation and Fragmentation in Sulfur and Oxygen Compounds

Table VI compares the heats of formation of analogous sulfur- and oxygen-containing ions, both for molecule ions and fragment ions. For the molecule ions the heats of formation of the oxygenated species are uniformly lower than the sulfur species, the differences being of the order of 6–19 kcal/mole. The CH_3S^+ ion has approximately the same heat of formation as the CH_3O^+ ion; however, reliable data are not available for the $C_2H_5O^+$ ion so a comparison cannot be made for the ethyl-substituted ion. The major and most striking differences lie in the heats of formation of the fragment ions formed by α cleavage, as shown by the differences $\Delta H_f(HSCH_2^+) - \Delta H_f(HOCH_2^+) = 44$ kcal/mole, $\Delta H_f(CH_3SCH_2^+) - \Delta H_f(CH_3OCH_2^+) = 35$ kcal/mole, and $\Delta H_f(CH_3CHSH^+) - \Delta H_f(CH_3CHOH^+) = 53$ kcal/mole. These differences clearly show that the ions derived by α cleavage are considerably more stable in the oxygen series than in the sulfur series.

Table VI. Heats of Formation of Oxygen- and Sulfur-Containing Ions

Ion	ΔH_f(ion), kcal/mole	
	$X \equiv S$	$X \equiv O$[a]
CH_3XH^+	215	202
CH_2XH^+	220	176
CH_3X^+	214	213
$C_2H_5XH^+$	204	185
CH_3CHXH^+	197	145
$C_2H_5X^+$	202	?
$CH_3XCH_3^+$	192	186
$CH_3XCH_2^+$	205	170
$C_2H_5XCH_3^+$	183	174

[a] Data for fragment ions from ref 2. Data for molecule ions based on ionization potentials reported in ref *12*.

The effect which these differences exert on the fragmentation patterns can be seen more clearly by comparing bond dissociation energies for fragmentation of the molecule ions. Assuming no activation energy for the reverse reaction, the bond dissociation energy should be approximately the activation energy for the fragmentation reaction. The energies for fragmentation of a number of molecule ions are compared in Table VII.

Table VII. Bond Dissociation Energies for Molecule Ions

Ion	Bond	Bond dissociation energy, kcal/mole $X \equiv S$	Bond dissociation energy, kcal/mole $X \equiv O$
CH_3XH^+	CH_3X^+–H	51	63
CH_3XH^+	$HXCH_2^+$–H	57	26
$C_2H_5XH^+$	$C_2H_5X^+$–H	50	?
$C_2H_5XH^+$	$HXCH_2^+$–CH_3	48	23
$C_2H_5XH^+$	$CH_3CH(XH)^+$–H	45	12
$CH_3XCH_3^+$	CH_3X^+–CH_3	54	59
$CH_3XCH_3^+$	CH_3XCH_2–H	65	36
$C_2H_5XCH_3^+$	$C_2H_5X^+$–CH_3	51	?
$C_2H_5XCH_3^+$	$CH_3XCH_2^+$–CH_3	54	28
$C_2H_5XCH_3^+$	CH_3X^+–C_2H_5	55	63

Several points are evident from the data in Table VII. The activation energies for fragmentation of the sulfur compounds by cleavage of an S–H or S–C bond (with charge intention on sulfur) are only slightly lower than the activation energy for cleavage of an α C–H or C–C bond. Thus the two fragmentation routes should be competitive, and experimentally (see Table I) one sees fragment ions originating by both routes.

On the other hand, cleavage of the O–H or O–C bond in the oxygen compounds has a considerably higher activation energy than that for α cleavage. Since the rate of the fragmentation reaction is strongly dependent on the activation energy, one would, therefore, expect to see only minor abundances of ions such as CH_3O^+ and $C_2H_5O^+$, and this is in agreement with the observed spectra (Table I).

The data of Table VII also explain the observation that the parent ions of mercaptans and sulfides are of greater abundance than the parent ions of the corresponding alcohol and ether. The parent ion abundance depends primarily on the activation energy for the lowest energy fragmentation reaction. For alcohols and ethers this route is α cleavage with an activation energy in the range 12–36 kcal/mol. For the mercaptans and sulfides both α cleavage and cleavage of the bond to sulfur have approximately the same activation energy; however, this activation energy is in the range 45–65 kcal/mole, some 30 kcal/mole higher than for the oxygen analogs.

The differences in the mass spectra of the sulfur and oxygen compounds have been attributed[1] to the greater ability of sulfur, compared to oxygen, to stabilize the positive charge in ions of the form RX^+. The present comparison shows that this effect is of only minor importance and that the major effect is the ability of the heteroatom to stabilize the ions formed by α cleavage. These ions, such as $RXCH_2^+$, are considered to be stabilized through donation of electrons from the heteroatom in the resonance form $RX^+{=}CH_2$. From the present results such resonance stabilization is much less effective for sulfur, presumably because of the greater size of the sulfur atom.

Finally, the data of Table VII allow us to make a rough estimate of $\Delta H_f(C_2H_5O^+)$, a value which does not appear to be obtainable directly by mass spectrometry. If we assume $D(CH_3O^+{-}H) - D(C_2H_5O^+{-}H) = D(CH_3S^+{-}H) - D(C_2H_5S^+{-}H)$, we can calculate $D(C_2H_5O^+{-}H) \approx 62$ kcal/mole, leading to $\Delta H_f(C_2H_5O^+) \approx 195$ kcal/mole. Similarly the assumption $D(CH_3O^+{-}CH_3) - D(C_2H_5O^+{-}CH_3) \approx D(CH_3S^+{-}CH_3) - D(C_2H_5S^+{-}CH_3)$ leads to $D(C_2H_5O^+{-}CH_3 \approx 56$ kcal/mole and $\Delta H_f(C_2H_5O^+) \approx 198$ kcal/mole. A value of 195–200 kcal/mole appears much more reasonable than the value of approximately 153 kcal/mole which has been derived[2] from the appearance potential of the ion nominally of $C_2H_5O^+$ structure from ethyl acetate.

Acknowledgments. The authors are indebted to the National Research Council of Canada for generous financial support. The award of a Province of Ontario Graduate Fellowship to B. G. K. is gratefully acknowledged.

Appendix

The following heats of formation (all in kcal/mole) were employed in this work. Deuterium-labeled species were assumed to have heats of formation identical with unlabeled species: H, 52.1;[16] CH_3, 32.1;[16] C_2H_3, 65.3;[16] C_2H_4, 12.5;[16] C_2H_5, 25.4;[16] C_3H_5 (allyl), 30.0;[16] c-C_3H_5, 53;[3] C_3H_6, 4.88;[16] CH_3SH, −5.46;[17] C_2H_5SH, −10.99;[17] i-C_3H_7SH, −18.19;[17] CH_3SCH_3, −8.94;[17] $CH_3SC_2H_5$, −14.22;[17] n-$C_3H_7SCH_3$, −19.51;[17] $(C_2H_5)_2S$, −19.92;[17] $(CH_3S)_2$, −5.71;[17] $(C_2H_5S)_2$, −17.78.[17]

---

(16) R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

(17) H. Mackle and P. A. G. O'Hare, *Tetrahedron*, **19**, 961 (1963).

Ion–Molecule Chemistry of Diborane by Ion Cyclotron Resonance

Robert C. Dunbar

Contribution from the Department of Chemistry, Stanford University, Stanford, California.

Received May 2, 1968

Abstract: Positive and negative ion–molecule chemistry of diborane has been investigated by ion cyclotron resonance. The production of a series of negative ions is described, and the reaction $BH_4^- + B_2H_6 \rightarrow B_2H_7^- + BH_3$ is studied in detail by double resonance: the three boron atoms in the reactants appear with equal probability in the neutral product. Several sulfur-containing negative ions are described, and an excited state of BH_4^- is shown to be produced from OH^-. A number of high-mass positive ions are found to be reactively formed by successive additions of B_2H_2 to ionic reactants.

Investigation of the chemistry of boron hydrides and related compounds has shown that their structure and behavior provide sharp contrasts to familiar organic systems.[1,2] However, except for the chemistry of several stable negative ions in solution, little is known of their ionic chemistry. Since ion cyclotron resonance (ICR) provides a powerful means of studying ion–molecule chemistry,[3–5] it is of interest to apply it to the study of boron-containing ions; the rapidly growing body of knowledge of a variety of ion–molecule reactions provides a valuable point of reference.[6] In general terms, the highly electron-deficient positive ions can be expected to show new patterns of structural and reactive behavior; on the other hand, many boron-containing negative ions are isoelectronic with organic systems, and it may be possible to interpret the chemistry of these ions using the methods and ideas of organic chemistry.

A preliminary study of diborane using single and double cyclotron resonance techniques is described in this paper. Previous work on gas-phase boron hydride ions has been done by conventional mass spectroscopic methods, using positive ions[7–9] produced by energetic electron impact, and more recently negative ions produced both by electron impact[10] and by high-energy Kr ions.[11] Aside from incidental observations,[8] ion–molecule reactions have been largely ignored. Ion cyclotron resonance spectrometry provides a convenient tool for examining ion–molecule reactions and in addition allows the production of ions by reactive mechanisms.

Experimental Section

Previous publications have described the ion cyclotron spectrometer used in this work and discussed its use in detecting positive ions and in identifying and characterizing the energy dependence of ion–molecule reactions.[12,13] The ionizing electron beam was normally run at 40 or 70 eV for low-pressure positive ion spectra (less than 10^{-6} torr); high-pressure positive ion spectra were taken using 17- or 18-eV electrons, except for the $B_2 \rightarrow B_3$ double resonance as discussed below. Negative ions were normally produced with about 8-eV electrons at pressures from 5×10^{-6} to 5×10^{-5} torr using an ionizing beam current of 3–10 μA. From the behavior of the spectra as a function of pressure, it is believed that some of the higher mass negative ions of diborane are formed from products of pyrolysis at the hot filament and accelerated into the analyzing cell by the electron beam accelerating potential. Thus the presence of a high-mass ion cannot be assumed, as is often done in the positive ion case, to be due to some ion–molecule reaction.

Diborane was synthesized by two methods. One sample was prepared by a convenient technique for which the author is indebted to Dr. William L. Jolly:[14] 1.6 g of KBH_4 (Metal Hydrides Inc.) was added slowly to a rapidly stirred sample of 30 ml of 85% phosphoric acid in an evacuated vacuum system, and the product was collected continuously by pumping through a Dry Ice–acetone trap into a liquid nitrogen trap. Several other samples were prepared by reduction of boron trifluoride etherate (Matheson Coleman and Bell, 47%) with $LiAlH_4$ in a flowing-nitrogen system.[15] All samples were purified by four to six passes through a CS_2 slush trap followed by pumping on the frozen sample. Frequent low-pressure spectra

---

(1) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(2) E. L. Muetterties, Ed., "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967.

(3) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(4) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967).

(5) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(6) For recent work and references see Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966.

(7) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, in Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961.

(8) A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 2428 (1966).

(9) E. J. Sinke, G. A. Pressley, Jr., A. B. Baylis, and F. E. Stafford, *J. Chem. Phys.*, **41**, 2207 (1964).

(10) R. E. Enrione and R. Rosen, *Inorg. Chim. Acta*, **1**, 169 (1967).

(11) G. Hortig, O. Mueller, K. R. Schubert, and E. Fluck, *Z. Naturforsch.*, **21b**, 609 (1966).

(12) J. L. Beauchamp and S. E. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

(13) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1968.

(14) W. L. Jolly, private communication.

(15) S. G. Shore, K. W. Boddeker, and J. A. Patton, *Inorg. Syn.*, **9**, 4 (1967).