Electron Impact Studies of Some Sulphides and Disulphides

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The appearance potentials of a number of radical ions produced on electron impact of organic sulphur compounds have been measured. In order to elucidate the rearrangement processes of the $(CH_3)_2S^+$ ion, a half-deuterated dimethyl sulphide has been synthesized and the appearance potentials and mass spectra studied. The significance of the measurements for bond-dissociation energy relationships in organic sulphur compounds is discussed.

In a study of the thermochemistry of some organic sulphides, Mackle and Mayrick [1] drew attention to Franklin and Lumpkin's electron impact measurements [2] on dimethyl sulphide and dimethyl disulphide and suggested that the electron impact processes (1) and (2) be re-studied.

$$CH_3SCH_3 + e \xrightarrow{A_1} CH_3 + SCH_3^+ + 2e, \tag{1}$$

$$CH_3SSCH_3 + e \xrightarrow{A_2} CH_3S + SCH_3^+ + 2e. \tag{2}$$

This paper reports such an investigation. A number of appearance potential measurements were also made for other sulphur compounds, in order to see if any consistent pattern emerged both for the ionization processes and for the bond-dissociation energies derived from appearance potentials. Since the commencement of this work, other workers [3, 4] have described investigations which overlap some of our material.

EXPERIMENTAL

MATERIALS

The following were available commercially: dimethyl sulphide, diethyl sulphide, di-n-propyl sulphide, dimethyl disulphide, diethyl disulphide, di-n-propyl disulphide. We are indebted to Dr. Mackle for samples of methyl phenyl sulphide and ethyl phenyl sulphide. Pure samples were obtained by repeated fractional distillation *in vacuo* until reproducible standard mass-spectrometric cracking patterns were obtained. 1,1,1,-trideutero dimethyl sulphide was synthesized from reaction of deuterated methyl iodide with sodium mercaptide. The deuterated methyl iodide was prepared by a modification of the method of Cotton *et al.*[5] Trimethyl oxosulphonium iodide (prepared according to Kuhn and Treschmann [6]) (1·79 g) was dissolved in 10 g D_2O and 0·0024 g K_2CO_3 (anhydrous) added. The solution was heated on a steam bath for 1 h, cooled at 0°C for 2 h, and the solid filtered off. Two further equilibrations on this solid product following the procedure given above yielded 0·71 g of the fully deuterated trimethyl oxosulphonium iodide. After drying, this compound was heated to 200°C, at a pressure of 20 mm Hg until all the solid had decomposed. The products were collected in a liquid-nitrogen-cooled trap, and vacuum distilled, followed by repeated bulb-to-bulb distillation. This resulted in 0·3 g deuterated methyl iodide (25 % yield based on trimethyloxosulphonium iodide, 67 % yield on the deuterated trimethyloxosulphonium iodide). The deuterated methyl iodide was vacuum-distilled on to excess sodium mercaptide,[7] kept at liquid-nitrogen temperature. The mixture was warmed slowly to room temperature, cooled to liquid-nitrogen temperature, rewarmed to room temperature, and the resultant product distilled into a liquid-nitrogen-cooled trap. After two further trap-to-trap distillations, retaining the middle fraction in each case, about 0·1 ml of product was collected in a mass-spectrometer sample tube.

Electron impact measurements were made using a Metropolitan-Vickers M.S.2 mass spectrometer fitted with an electrostatically variable slit at the collector. The appearance potentials were calculated as described by Majer, Patrick and Robb.[8] The calibrating gases were argon and krypton. In the measurement of all the appearance potentials, the ion efficiency plot was parallel to that for the calibrating gases except where the value is stated to be inaccurate.

RESULTS AND DISCUSSION

The mass spectra of aliphatic thioethers was studied by Levy and Stahl.[9] They found that, in addition to the direct bond fission at carbon atoms α and β to the sulphur atom providing ions of the type RS^+ and $RSCH_2^+$, a number of rearrangement processes occurred. The commonest of these was responsible for the production of ions of the type RSH^+ and RSH_2^+, where R is an alkyl radical or a hydrogen atom. Rearrangements analogous to these have been observed in the mass spectra of aliphatic ethers, but the ions are of much lower abundance. It is possibly due to the complex nature of the processes occurring subsequent to ionization that electron-impact studies upon aliphatic thioethers have been found difficult to interpret. The reproducibility of appearance potentials was found in the present study to be less than that observed with other series of related compounds and there are a number of discrepancies between the values quoted by different groups of workers.

TABLE 1

process	dimethyl sulphide				trideutero dimethyl sulphide			
	ion	m/e	% abundance	A.P., eV	ion	m/e	% abundance	A.P., eV
ionization	$(CH_3)_2S^+$	62	100·0	9·0	$CH_3SCD_3^+$	65	100·0	8·7
β-cleavage	$CH_3SCH_2^+$	61	36·3	—	$CH_2SCD_3^+$	64	27·4	—
					$CH_3SCD_2^+$	63	13·3	—
α-cleavage					CD_3S^+	50	4·7	11·15
					CD_2HS^+	49	7·4	11·55
					CDH_2S^+	48	21·7	11·05
	CH_3S^+	47	108·3	11·3	CH_3S^+	47	62·1	11·0
α- and β-cleavage	CH_2S^+	46	43·1	—	CH_2S^+	46	46·7	—
					CDS^+			
	CHS^+	45	50·4	—	CHS^+	45	27·2	—
rearrangement					SD_3^+	38	3·3	14·8
					SHD_2^+	37	17·7	13·9
					SH_2D^+	36	17·3	12·8
	SH_3^+	35	39·4	13·85	SH	35	3·0	11·9
					$C_2D_3^+$	30	4·0	12·1
					$C_2D_2H^+$	29	16·7	13·5
					$C_2DH_2^+$	28	11·5	15·05
	$C_2H_3^+$	27	24·3	14·7	$C_2H_3^+$	27	1·1	16·7
α-cleavage	CH_3^+	15	6·5	13·0	CH_3^+	15	5·9	13·1

The appearance potentials for trideuterodimethyl sulphide (CD_3SCH_3) and dimethyl sulphide and comparison of their mass spectra are given in table 1. SH_3^+ and SD_3^+ are produced in almost equal abundance but the ions SD_2H^+ and SDH_2^+ are both produced at four times the rate of the mono-isotopic species. This suggests that the most favoured process by which SH_3^+ is formed from dimethyl sulphide involves the migration of hydrogen atoms from both of the carbon atoms. An alternative rearrangement process involving the elimination of SH_3 results in the formation of the ion $C_2H_3^+$, the peak at mass 27 being of high relative intensity. Again when the mass spectrum of the labelled thioether is examined, it is the polyisotopic species, $C_2HD_2^+$ and $C_2H_2D^+$ which have the greatest abundance, the monoisotopic species providing only minor mass peaks. No reliable conclusions can be drawn from the wide variation in the value of the appearance potentials for these fragments.

The most unambiguous results are those obtained from the measurements of the appearance potential of the methyl radical ion. The relative intensities of the peaks at mass 15 for both thioethers are approximately the same, suggesting that little rearrangement takes place and the value of the appearance potential is within experimental error the same in both cases (13·0 eV). Combination of this value with that for the ionization potential of the methyl radical [10] (10 eV) gives an upper limit for the bond dissociation energy (CH_3S—CH_3) of 69 ± 2 kcal mole^{-1} (an upper limit because $I(CH_3) > I(CH_3S)$. Unfortunately, because of the superposition of the mass peaks due to the ions CD_3^+ and H_2O^+ from the blank spectrum of the instrument, no value for the appearance potential of CD_3^+ can be measured. The isotope effect is clearly demonstrated in the mass spectrum of trideutero dimethyl sulphide, where the frequency of rupture of the C—D bond is about one half of that of the C—H bond. Far more unexpected, however, is the difference in the rate of cleavage of the C—S bonds where the rate of rupture of the S—CD_3 bond is 12 times the rate for the S—CH_3 bond.

In addition, there are rearrangement processes leading to the formation of SCD_2H^+ and $SCDH_2^+$. Because of the possibility of several isotopic contributions in the mass peaks 48 and 49 the difference between the measured appearance potential of these two peaks and the appearance potential of the 47(SCH_3^+) peak in the mass spectrum of dimethyl sulphide may not be significant. It suggests, however, that the rearrangement process does not involve any great amount of energy. The appearance potentials of both the 47(CH_3S^+) and 50(CD_3S^+) peaks in the mass spectra of trideutero dimethyl sulphide are lower than that of the 47(SCH_3^+) from dimethyl sulphide, suggesting that the appearance potential of the fragment corresponding to the rupture of a C—S bond alone should be about 0·2 eV less than the previously accepted values. The appearance potential for CH_3S^+ in dimethyl sulphide is given by Franklin and Lumpkin[2] as 11·38 eV and by Palmer and Lossing [4] as 11·24 eV, both in good agreement with our value of 11·3 eV which leads to $D(CH_3S$—$CH_3)$ = 74 kcal mole^{-1}. This value is higher than the above mentioned upper limit of 69 kcal mole^{-1}.*

The other significant rearrangement process is that leading to the formation of the ion SH_3^+. Here again the examination of the mass spectra of trideutero dimethyl sulphide showed that it was not a simple process.

The results for diethyl sulphide are listed in table 2.

Probably as for dimethyl sulphide, many of these mass peaks are composite with contributions due to ions arising by more than one process. This is almost certainly the case for the ion CH_3S^+ where the plot of ion current against electron accelerating voltage is not straight. Our value for the ionization potential (8·6 eV) is consistent with the photo-ionization value [11] (8·48 eV) and that of Hobrock and Kiser,[22] but is less than that quoted by others using the electron-impact method. α-Cleavage leading to the $C_2H_5S^+$ ion is a favoured process and good agreement exists between our value (11.05 eV) and those of other workers [2] (11·15 eV), with the exception of Hobrock and Kiser [22] who quote a value of 12·0 eV. Combination of our value with the ionization

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* Recently Hobrock and Kiser [22] using a slightly different method have quoted a value of 11·7 eV for $A(CH_3S^+)$.

TABLE 2

dissociative process	diethyl sulphide		di-n-propyl sulphide		phenyl methyl sulphide		phenyl ethyl sulphide		dimethyl disulphide		diethyl disulphide	
	ion formed	A.P., eV	ion formed	A.P., eV	ion formed	A.P., eV	ion formed	A.P., eV	ion formed	A.P.,eV	ion formed	A.P.,Ve
ionization	$(C_2H_5)_2S^+$	8·6	$(C_3H_7)_2S^+$	8·95	$C_6H_5SCH_3^+$	8·9	$C_6H_5S^+C_2H_5$	8·8	$(CH_3S)_2^+$	9·05	$(C_2H_5S)_2^+$	8·85
α-cleavage	$C_2H_5S^+$	11·05	$C_3H_7S^+$	11·55	$C_6H_5S^+$	12·15	$C_6H_5S^+$	12·2	CH_3SS^+	11·45	$C_2H_5SS^+$	11·5
			$C_3H_7^+$	12·0	C_6H^+	14·4	$C_2H_5^+$	13·7			C_2H^+	11·35
β cleavage	$C_2H_5SCH_2^+$	10·65	$C_3H_7SC_2H_2^+$	10·9			$C_6H_5SCH_2^+$	11·7				
γ cleavage			$C_3H_7SC_2H_4^+$	11·55								
symmetrical cleavage									CH_3S^+	11·1	$C_2H_5S^+$	11·15
rearrangement	$C_2H_5SH^+$	10·4	$C_3H_7SH^+$	10·4	$C_7H_7^+$	12·0	$C_6H_5SH^+$	11·4	$CH_3SCH_2^+$	11·0	$C_2H_5SSH^+$	10·9
	CH_3S^+	12·75	$C_2H_5S^+$	12·2	C_6H^+	12·0	CHS^+	12·5	CH_3SH^+	11·2	$C_2H_4S^+$	11·6
			CH_3S^+	12·65	CHS^+	14·5			CHS^+	13·6	$HSSH^+$	11·9

potential of the C_2H_5S radical [2] (8·15 eV) gives $D(C_2H_5S—C_2H_5)$ as 2·9 eV or 67 kcal mole^{-1}. Franklin and Lumpkin's value for I(EtS) may be too high since it should be lower than that of I(MeS) for which the recorded value is 8·06 eV. Although the value for the appearance potential of the $C_2H_5^+$ ion is less certain, combination with the ionization potential of the ethyl radical (8·78 eV [12]) gives a value of similar magnitude. The ion responsible for the ***m/e*** 62 peak must be $C_2H_5SH^+$ corresponding to ethylene elimination from the molecule ion. From the known heats of formation of the molecules [13] and the ionization potential of C_2H_5SH[14] an apparent heat of formation of ethylene may be calculated using the equation:

$$A(C_2H_5SH^+) = \Delta H_f(C_2H_5SH)+I(C_2H_5SH)$$
$$+\Delta H_f(C_2H_4)-\Delta H_f[(C_2H_5)_2S]$$

This gives a value of +18·8 kcal mole^{-1} compared with the literature value [15] of 12·496 kcal mole^{-1}.

Despite the complex rearrangement process which must take place to provide the CH_3S^+ ion from $(C_2H_5)_2S^+$, the energy associated with this process is small. The discrepancy is analogous to that observed in the elimination of CO from benzoyl compounds [16] and CF_2 from aromatic compounds with a CF_3 side-chain [17] and may be considered as representing the activation energy for the back reaction which reconstitutes the original molecule.

α-Cleavage in di-n-propyl sulphide leads to the formation of the ions $C_3H_7^+$ and $C_3H_7S^+$. The appearance potential of the former ion when combined with the most recent value of the ionization potential of the n-propyl radical (8·68 eV) [18] leads to a value of $D(C_3H_7—SC_3H_7)$ of 3·3 eV or 76 kcal mole^{-1}. However, $I(n-C_3H_7)$ has been measured in several ways and the results are either in good agreement with the most recent value or 1 eV less. $I(n-C_3H_7S)$ is not known but on analogy with $I(CH_3S^+)$ and $I(C_2H_5S^+)$ would be expected to have a value of about 8 eV. Combining this with the measured appearance potential of $C_3H_7S^+$ gives a second value of $D(C_3H_7—SC_3H_7)$ of 3·55 eV or 80 kcal mole^{-1}. It is probable that excess energy is involved in the formation of these ions; their size and complexity permitting internal reorganization.

The appearance potential of the ion $n-C_3H_7S.CH_2CH_2^+$ formed by β-cleavage is very close to that of the ion $C_2H_5S.CH_2CH_2^+$ formed in an analogous process from $(C_2H_5)_2S$. The energy associated with the rearrangement processes leading to the formation of the CH_3S^+ and $C_2H_5S^+$ ions is small in both cases considering the complexity of the process (*ca.* 4 eV). No calculations can be made because of the uncertainty associated with the structure of both ionized and unionized fragments. In the rearrangement ion n-$C_3H_7SH^+$, however, a value for the apparent heat of formation of the unionized fragment may be made using the equation

$$A(C_3H_7SH^+) = I(C_3H_7SH^+) + \Delta H_f(C_3H_7SH) + \Delta H_f(C_3H_6) - \Delta H_f(C_3H_7)_2S.$$

The calculated value for $\Delta H_f(C_3H_6) = 0{\cdot}64$ eV or +15 kcal mole^{-1}. This is again considerably in excess of the accepted value and includes an energy of reorganization.

α-Cleavage in phenyl methyl sulphide leads to the formation of $C_6H_5S^+$ and the measured value of the appearance potential of this ion is in agreement with the recent value (12·1) of Palmer and Lossing.[4] As pointed out by Lossing, the combination of this appearance potential with the ionization potential of the C_6H_5S radical leads to a value of 83 kcal mole^{-1} which is more than 20 kcal in excess of the value proposed by Sehon. Although with acetophenone [16] no rearrangement of atoms occurs in the formation of the benzoyl ion, nevertheless in the present case the high value of $D(C_6H_5S{-}CH_3)$ may be due to a rearrangement process which could only be detected by isotopic labelling.

Some support for this assumption arises from the abundance of rearrangement ions of the type $C_7H_7^+$ and $C_6H_6^+$ having the same low appearance potential of 12·0 eV and the very high appearance potential of the $C_6H_5^+$ ion. If this could be identified as the phenyl ion, formed in a simple α-cleavage process, then the excess energy in the process would be almost as great as that required to break the ($C_6H_5{-}S$) bond.

The appearance potential of the $C_6H_5S^+$ ion from phenyl ethyl sulphide is close to that observed for phenyl methyl sulphide and so the foregoing comments apply also to the dissociation of this molecule. A rearrangement process leads to the formation of the thiophenyl ion C_6H_5SH and permits the calculation of an apparent heat of formation of ethylene using the relationship:

$$A(C_6H_5SH^+) = \Delta H_f(C_6H_5SH) + I(C_6H_5SH) + \Delta H_f(C_2H_4) - \Delta H_f(C_6H_5SC_2H_5),$$

and the heats of formation given by Cox [13] together with the ionization potential obtained by Baba *et al.*[19] The value of 2·5 eV or 58 kcal mole^{-1} for $\Delta H_f(\text{app})C_2H_4$ is about 25 kcal mole^{-1} in excess of the accepted value of +12·5 kcal mole^{-1} and this excess may be considered as an energy of reorganization within the ethylene molecule.

The measured ionization potential of dimethyl disulphide is higher than the photoionization values quoted by Varsel *et al.*[20] (8·53 eV) and Watanabe (8·46 eV), but agrees with that of Hobrock and Kiser [3] (9·1 ± 0·2 eV). The value obtained for the appearance potential of the ion CH_3S^+ produced by symmetrical cleavage is in good agreement with those measured by Lossing [4] and by Franklin and Lumpkin [2] but differs considerably from that of Hobrock and Kiser [3] of 13·0 ± 0·4 eV.

In diethyl disulphide, the semilog plots for the ions $C_2H_5SS^+$ and $C_2H_5^+$ are not straight suggesting multiple contributions upon the mass peaks. Symmetrical cleavage leading to the formation of the ion $C_2H_5S^+$ has an appearance potential of 11·15 eV, in good agreement with previous values and suggesting $D(C_2H_5S{-}SC_2H_5)$ as 69 ± 2 kcal mole^{-1}. The most interesting rearrangement process is that leading to the ion $HSSH^+$ and it has been suggested [3] that the heat of formation of this ion can be estimated from its appearance potential and the heats of formation of ethylene and diethyl disulphide. It was shown here and previously [16] that this is not a justifiable procedure. Similar reasoning applies to the rearrangement ion $C_2H_5SSH^+$. The above appearance potentials for the following peaks are in good agreement with the values of Hobrock and Kiser[3] given in parentheses 94(10·8), 66(12·2). However, further peaks are in poor agreement 122(8·30), 61(12·5), 60(12·3), 29(14·2).

By combining appearance potentials of the alkyl thio-ions (RS^+) from the di-alkyl sulphides and the di-alkyl disulphides the difference in the values of the bond dissociation energies of the pairs of compounds may be obtained independently of the value of $I(RS)$. The value of $D(CH_3S—SCH_3) - D(CH_3S—CH_3)$ obtained in this work was $-4{\cdot}5 \pm 4{\cdot}5$ kcal mole^{-1} compared with the value $-2{\cdot}5 \pm 4{\cdot}5$ kcal mole^{-1} obtained by Palmer and Lossing. This is in contrast to the value of $D(C_2H_5S—SC_2H_5) - D(C_2H_5S—C_2H_5)$ of $+2{\cdot}3 \pm 4{\cdot}5$ kcal mole^{-1} obtained in this work. This discrepancy is probably due to the complication of rearrangement processes leading to the formation of the RS^+ ions and stresses the need for kinetic determinations of the relative strengths of the two types of bond (C—S and S—S). These considerations apply with equal force to the calculations of the heats of formation of the alkyl thio-radicals from their appearance potentials and the heats of formation of the molecules. Thus, while the value for $\Delta H_f(CH_3S)$ calculated from the present results is in agreement with previous values, it is almost certainly high by at least 3-5 kcal.

The only appearance potential of an ion formed by simple cleavage of the di-n-propyl disulphide ion, which could be measured, was that of the $C_3H_7^+$ ion. If this were produced without rearrangement then combination of the value of 11·2 eV with that of $I(n\text{-}C_3H_7)$[21] gives $D(n\text{-}C_3H_7SS\text{-}C_3H_7)$ = 59 kcal mole^{-1}. Again there was an elimination process with an olefin as the unionized fragment. The appearance potential of the ion formed by the loss of C_3H_6 was 11·4 eV and that due to the loss of C_6H_{12} was 12·2 eV. These values are close to those obtained for the appearance potentials of analogous ions from diethyl disulphide.

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