Reactions of Thermal Energy Ions

Part 5.*-Ion-Molecule Reactions in Hydrogen Sulphide

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The formation of H_3S^+ in the high-pressure mass spectrum of hydrogen sulphide has been shown to be due to the two concurrent ion-molecule reactions:

$$H_{2}S^{+}+H_{2}S \xrightarrow{1} H_{3}S^{+}+SH$$
$$HS^{+}+H_{2}S \xrightarrow{2} H_{3}S^{+}+S.$$

The cross-sections and rate constants for these reactions have been measured at a field strength of 10.5 V cm⁻¹ (corresponding to an ion exit energy of 3.7 eV) when values of 2.1×10^{-10} and 2.6×10^{-10} molecule⁻¹ cm³ sec⁻¹ were obtained for k_1 and k_2 respectively. Using a pulsing technique the rate constants for thermal energy ions were measured and values of 2.8×10^{-10} and 3.6×10^{-10} obtained for k_1 and k_2 . These have been compared with values calculated from the simple ioninduced dipole model.

Recent work on ion-molecule reactions in water ¹ and in ammonia ² has shown that the formation of the H_3O^+ and NH_4^+ ions in these systems is not due to simple reactions involving only the parent molecular ions, i.e.,

$$\begin{split} &H_2O^+ + H_2O \rightarrow H_3O^+ + OH, \\ &NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2, \end{split}$$

but at higher electron energies the product ions are formed by proton transfer reactions involving the OH^+ and NH_2^+ ions, i.e.,

$$OH^+ + H_2O \rightarrow H_3O^+ + O$$
$$NH_2^+ + NH_3 \rightarrow NH_4^+ + NH_3$$

The presence of the H_3S^+ ion in the high-pressure mass spectrum of hydrogen sulphide has been attributed ³ to the reaction

$$H_2S^+ + H_2S \rightarrow H_3S^+ + SH.$$

In view of the role of OH^+ and NH_2^+ in the formation of the secondary ion in water and ammonia it seemed of interest to study the possibility of the HS^+ ion similarly reacting by a proton-transfer process with hydrogen sulphide to form the protonated ion H_3S^+ .

In studies of ion-molecule reactions by the conventional internal ionization technique the reactant ions undergo continuous acceleration by the electric field needed to withdraw the ions for analysis. Hence the cross-sections (and rate constants) measured under these conditions represent a weighted average for ions having energies from zero to the final ion exit energy which is determined by the repeller

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^{*} part 4, see ref. (2).

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field strength and the distance which the ion travels. The dependence of the rate constant for the ion-molecule reaction upon the ion velocity or field strength has been discussed and various studies have yielded results in disagreement, especially at low field strengths.⁴⁻⁷ The reaction of ions under thermal conditions (i.e., zero-field strength) can be studied using the pulsed mode of operation of the internal ionization method. In this technique ^{8, 9} a short pulse of electrons is passed through the ion source (which is at zero field) and in the normal manner produces primary ions by electron impact with the molecules in the source. A known and variable time later a voltage pulse is applied to the repeller plate to expel the ions from the ion source for analysis. In the interval between the ionizing pulse and the withdrawal pulse the ions react with the molecules under virtually thermal conditions and consequently reaction rates may be determined. Accordingly we have studied ion-molecule reactions in hydrogen sulphide (*a*) in the presence of an applied field of 10.5 V/cm, and (*b*) at zero-field strength using the pulsing technique.

EXPERIMENTAL

The modified AEI Ltd., MS 2 mass spectrometer described previously ⁹ was used. The cross-sections and rate constants for the individual reactions were measured at 10.5 V cm⁻¹ repeller field strength (corresponding to an ion-exit energy of 3.7 eV) using the ratio plot method.¹⁰⁻¹² The electron beam was pulsed (pulse duration 0.1-1.0 µsec with a repetition rate of about 2×10^5 pulses sec⁻¹) with a constant repeller field, so that space-charge effects are minimized. Thermal constants were measured using the pulsed source technique.⁹

Hydrogen sulphide was obtained from a cylinder (Matheson Co.) and used without further purification. The pressure of the gas in the inlet reservoir was measured using an Atlas-Wecke type MC Torrmeter calibrated against a dibutyl-phthalate manometer.

RESULTS AND DISCUSSION

The H_3S^+ ion is formed by a bimolecular process in the high pressure mass spectrum of hydrogen sulphide. Because of the similarity of the appearance potentials of H_2S^+ and H_3S^+ (10.50 and 10.6 eV, respectively) the ion-molecule reaction leading to the formation of the H_3S^+ ion is said to be ³

$$H_2S^+ + H_2S \rightarrow H_3S^+ + SH.$$

This method of correlation of appearance potentials to identify the reactant ion is only valid when the secondary ion is produced by a reaction involving only one primary ion. In the mass spectrum of hydrogen sulphide the HS⁺ ion is a significant primary ion and its appearance potential ¹³ is appreciably higher (14.4 eV) than that of H_2S^+ ,

$$HS^+ + H_2S \xrightarrow{2} H_3S^+ + S.$$

One criterion for the occurrence of an ion-molecule reaction is that it is exothermic or thermoneutral. Field and Franklin ^{14, 15} have reported values of 236 and <187 kcal mole⁻¹ for the heats of formation of H₂S⁺ and H₃S⁺ respectively. Palmer and Lossing ¹³ have measured $\Delta H_f(\text{HS}^+)$ as ≤ 276 kcal mole⁻¹. Using these values in conjunction with $\Delta H_f(\text{H}_2\text{S}) = -4.8$ kcal mole⁻¹, $\Delta H_f(\text{HS}) = 32$ kcal mole⁻¹ and $\Delta H_f(\text{S}) = 66$ kcal mole⁻¹ we find that reactions (1) and (2) are exothermic by 12 and 18 kcal mole⁻¹ respectively, and on the basis of their thermochemistry are both capable of contributing towards the formation of the H₃S⁺ ion at energies above the appearance potential of HS⁺.

DETERMINATION OF CROSS-SECTIONS AND RATE CONSTANTS

RATIO PLOT METHOD

In fig. 1, curve 1, is shown the $I_{H_3S^+/H_2S^+}$ ratio as a function of the nominal electron energy at a constant repeller voltage of 10.5 V cm⁻¹ and a hydrogen sulphide source concentration of 4.46×10^{13} molecules cm⁻³. From the appearance of the H₃S⁺ ion at 5.7 eV nominal electron energy to 9 eV the ratio is, within experimental error, constant. At this energy the ratio begins to increase; this increase can be correlated with the formation of the HS⁺ ion, also shown in fig. 1 (curve 2) and shows that the HS⁺ ion is contributing significantly to the formation of the H₃S⁺ ion.



FIG. 1.—Curve 1, $I_{H_3S^+}/I_{H_2S^+}$ against nominal electron energy (V); curve 2, I_{HS^+} against nominal electron energy. Ordinate for curve 2 given on r.h.s.

For the two concurrent reactions (1) and (2) studied under conditions of constant ion acceleration, the total secondary ion current $I_{H_3S^+}$ is given by eqn. (3),

$$I_{\rm H_3S^+} = I_{\rm H_2S^+}Q_1[\rm H_2S]d + I_{\rm HS^+}Q_2[\rm H_2S]d + 4.19 \times 10^{-2}I_{\rm HS^+} + 0.74 \times 10^{-2}I_{\rm H_2S^+}.$$
 (3)

where Q_x is the macroscopic cross-section for reaction X, d is the distance the reactant ion travels in the ion source and [H₂S] refers to the source concentration in molecule cm⁻³. In formulating eqn. (3) the small differences in collection efficiencies have been neglected, and the last two items are isotopic corrections because of the contributions of the HS³⁴ and H₂S³³ ions towards the total ion current at m/e = 35.

Division of eqn. (3) by $I_{H_2S^+}$ yields the following equation:

$$I_{\rm H_3S^+}/I_{\rm H_2S^+} = (0.74 \times 10^{-2} + Q_1[\rm H_2S]d) + (I_{\rm HS^+}/I_{\rm H_2S^+})(4.19 \times 10^{-2} + Q_2[\rm H_2S]d)$$
(4)

which predicts that a plot of $I_{H_3S^+}/I_{H_2S^+}$ against $I_{HS^+}/I_{H_2S^+}$ should yield a straight line with the cross-sections Q_2 and Q_1 being obtainable from the slope and the intercept respectively.

Fig. 2, curve 1, shows a typical result obtained for hydrogen sulphide at $10.5 \text{ V} \text{ cm}^{-1}$ repeller voltage (corresponding to 3.7 eV ion exit energy), plotted in terms of eqn. (4). The ion current ratios were varied by changing the energy of the ionizing electrons. The good straight line and the non-zero intercept and slope (after correction for the isotopic contributions) shows that reactions (1) and (2) are occurring.

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Our results yield values of $9\cdot1\pm0\cdot3\times10^{-16}$ for Q_1 and $11\cdot4\pm0\cdot5\times10^{-16}$ for Q_2 , both in molecule⁻¹ cm². The limits of error represent the mean deviation of a number of runs and the experimental cross-sections were obtained by a least-squares analysis of the data. The rate constants have been calculated from the relation $k = Qd/\tau$, where τ is the residence time of the primary ion. Values of $2\cdot08\pm0\cdot07\times10^{-10}$ and $2\cdot64\pm0\cdot11\times10^{-10}$ have been obtained for k_1 and k_2 respectively (both in molecule⁻¹ cm³ sec⁻¹).



FIG. 2.—Curve 1, $I_{H_3S^+}/I_{H_2S^+}$ against $I_{HS^+}/I_{H_2S^+}$; curve 2, $I_{H_3S^+}/I_{H_2S^+}$ against nominal electron energy (V). Abscissa for curve 2 given on upper scale.

In fig. 2, curve 2 (different x-axis), is also shown a plot of of $I_{H_3S^+}/I_{H_2S^+}$ at electron energies below the appearance potential of HS⁺. The independence of this ratio with changing electron energy indicates that in this region only reaction (1) is contributing to the formation of the H₃S⁺. The values of Q_1 and k_1 obtained from several runs of the type in curve 2 are $Q_1 = 9.0 \pm 0.2 \times 10^{-16}$ molecule⁻¹ cm² and $k_1 = 2.06 \times 10^{-10}$ molecule⁻¹ cm³ sec⁻¹ and are in good agreement with values of 9.1×10^{-16} and 2.08×10^{-10} found for Q_1 and k_1 by the ratio plot method above using a wide range of electron energies.

Our data indicate that proton-transfer (reaction (2)) is favoured over hydrogen transfer (reaction (1)) by a factor of about 1.3 and, if the number of available hydrogen atoms, i.e., two, is taken into account, then the ratio is appreciably in favour of reaction (2).

PRESSURE VARIATION METHOD

Lampe et al.³ have reported a value of 3×10^{-10} molecule⁻¹ cm³ sec⁻¹ for k_1 by measuring the $I_{\rm H_3S^+}/I_{\rm H_2S^+}$ ratio as a function of pressure at 50 eV. Our work, using the ratio plot technique, has shown that the formation of the H₃S⁺ ion at 50 eV is not a simple reaction and consequently the value obtained by the pressure plot method reflects a composite rate constant for reactions (1) and (2). For comparison we have made a similar plot of the $I_{\rm H_3S^+}/I_{\rm H_2S^+}$ ratio versus source pressure for hydrogen sulphide at 50 eV, and our results are shown in fig. 3. Using the relations, $I_{\rm HS^+}/I_{\rm H_2S^+} = \overline{Q}[H_2S]d$, and $k = \overline{Q}d/\tau$, where \overline{Q} and \overline{k} are the quantities

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referring to the apparent reaction (1), we find that $\overline{Q} = 13 \cdot 3 \times 10^{-16}$ molecule⁻¹ cm² and $\overline{k} = 3 \cdot 04 \times 10^{-16}$ molecule⁻¹ cm³ sec⁻¹. Our value for \overline{k} is in good agreement with the value of $3 \cdot 0 \times 10^{-10}$ obtained by the pressure-plot study of Lampe *et al.*³



 H_2S reservoir pressure, mm Hg FIG. 3.— $I_{H_1S^+}/I_{H_2S^+}$ against H_2S inlet reservoir pressure (mm Hg).

We can make a direct comparison of \overline{Q} and \overline{k} with the values of Q and k we have established above by the ratio plot method for reactions (1) and (2). The following relationships exist between \overline{Q} , Q_1 and Q_2 and between \overline{k} , k_1 and k_2 :

 $\overline{Q} = \overline{Q}_1 + (I_{\text{HS}} + \overline{Q}_2 / I_{\text{H}_2\text{S}^+})$ and $\overline{k} = k_1 + (I_{\text{HS}} + k_2 / I_{\text{H}_2\text{S}^+}).$

The ratio $I_{H_3S^+}/I_{H_2S^+}$ measured at 50 eV has a value of 0.33. Using this in conjunction with the cross-sections and rate constants given in table 1 for reactions (1) and (2),

Table 1.—Cross-sections Q and rate constants k for ion-molecule reactions

reaction	Q	^k 10·5 V/cm	k _{thermal}	$\frac{k_{\rm thermal}}{k_{\rm 10.5 \ V/cm}}$	* k _{theory}	ref.
$H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	9·1±0·3	2.1	2.8	1.33	10·4	this work
$HS^++H_2S\rightarrow H_3S^++S$	11·4±0·5	2.6	3.6	1.36	10.5	,,
$H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	13.3	3.0			10.4	39
$H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	30	3 ·0			10.4	3
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	19.3	6.0	4.9	0.82	12.2	1
$OH^+ + H_2O \rightarrow H_3O^+ + O$	18.3	5.9	4.7	0.86	12.4	1
$D_2O^+ + D_2O \rightarrow D_3O^+ + OD$	11.8	3.5	3.7	1.06		1
$OD^++D_2O\rightarrow D_3O^++O$	8∙4	2.6	2.3	0.82		1
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	24.7	7.7	5.2	0.68	10.6	2
$NH_{7}^{+} + NH_{3} \rightarrow NH_{4}^{+} + NH$	16.0	5.1	3.4	0.67	10.8	2
$CH_{4}^{+} + CH_{4} \rightarrow CH_{5}^{+} + CH_{3}$	21.8	7.6	6.1	0.80	13.4	18
$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$	15.6	6.4	4·7	0.73	11.9	18
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units of $Q: 10^{16} \times \text{molecule}^{-1} \text{ cm}^2$; units of $k: 10^{10} \times \text{molecule}^{-1} \text{ cm}^3 \text{ sec}^{-1}$.

* calculated on the basis of ion-induced dipole interactions only.

† results based on pressure plot at 50 V electron energy.

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we find that $\overline{Q} = 12.9 \times 10^{-16}$ molecule⁻¹ cm² and $\overline{k} = 2.95 \times 10^{-10}$ molecule⁻¹ cm³ sec⁻¹, which are in excellent agreement with our directly measured values mentioned above.

PULSED (i.e., ZERO-FIELD) METHOD

The cross-sections and rate constants reported above have been measured at a constant field strength and 10.5 V cm⁻¹ and the ions which react have a range of energies from zero to 3.7 eV. Consequently the rate constants are not those corresponding to the rates for thermal energy ions for reactions (1) and (2). These could be obtained if the dependence of the cross-section on the ion velocity was known. This information is not easily obtainable because a study of the variation of Q with ion exit energy coupled with extrapolation of Q to zero-field has dubious validity. This has been attributed ¹⁶ to space-charge and mass discrimination effects at low repeller voltages. The thermal (or zero-field) rates can be measured directly by the pulsing technique, since in the time interval or delay time (0.1-1.6 μ sec) between the ionizing pulse and the ion-withdrawal pulse, the ions react with molecules under field-free conditions and from the variation of the product to reactant ion ratios with the delay time their rate of reaction under thermal conditions can be obtained.

For two concurrent reactions (1) and (2), the secondary ion current $I_{H_3S^+}$ observed after a time interval t between the pulses can be expressed (neglecting small differences in collection efficiencies) as the sum of the two independent contributions :

$$I_{\rm H_3S^+} = (k_1[\rm H_2S]I_{\rm H_2S^+} + k_2[\rm H_2S]I_{\rm HS^+})t + C, \tag{5}$$

where C is a constant representing the H_3S^+ formed by the ion-molecule reactions occurring during the ionizing and withdrawal pulses. Rearrangement of this equation gives

$$I_{\rm H_3S^+}/I_{\rm H_2S^+} = \{k_1[\rm H_2S] + (k_2[\rm H_2S]I_{\rm HS^+}/I_{\rm H_2S^+})\}t + C^1.$$
(6)

This expression predicts a linear relationship between $I_{H_3S^+}/I_{H_2S^+}$ and reaction time at constant electron energy when the source pressure is constant, provided the extent of reaction is small. The $I_{H_3S^+}/I_{H_2S^+}$ ratio was varied by changing the ionizing energy and, over the range of the delay times used, remained constant for constant electron energy.

In fig. 4 are plotted our delay curve data in terms of eqn. (6) for a range of uncorrected electron energies (10.0-14.7 eV) where $I_{HS^+}/I_{H_2S^+}$ is zero or very near to zero. The slopes of these delay-time curves are given in table 2, and are plotted

electron energy (eV)	10.0	1 0 ·3	10·5	10·7	10.9	11.2	11.4	11.7
$slope \times 10^{-4}$	1.20	1.23	1.18	1.17	1.30	1.27	1.25	1.27
$I_{\rm HS^+}/I_{\rm H2S^+}$	0	0	0	0	0	0	0	0
electron energy	12·0	12.1	12.3	12.8	13.0	13.3	13.5	13.7
$slope \times 10^{-4}$	1.24	1.25	1.22	1.26	1.22	1.24	1.22	1.26
$I_{\rm HS^+}/I_{\rm H2S^+}$	0	0	0	0.003	0.003	0.007	0.010	0.016
electron energy	14·0	14.2	14.5	14.7	15.0	19.0	20.0	22.0
$slope \times 10^{-4}$	1.24	1.30	1.31	1.27	1.32	1.57	1.54	1.64
$I_{\rm HS^+}/I_{\rm H2S^+}$	0.025	0.030	0.047	0·0 48	0.028	0.223	0.243	0.270
electron energy	25	28	30	32	38	46	47.5	48
$slope \times 10^{-4}$	1.62	1.79	1.78	1.81	1.83	1.87	1.68	1.92
$I_{\mathrm{HS}^+}/I_{\mathrm{H}_2\mathrm{S}^+}$	0.300	0.335	0 ·309	0.330	0.365	0.340	0.334	0.341

Table 2.—Delay curve data:
$$[slope = k_1 + (I_{HS}+k_2)/I_{H_2S}+]$$

all electron energies are uncorrected.



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10² I_{H3}S⁺/I_{H2}S⁺



delay time t (µsec)

FIG. 5.— $I_{H_3S^+}/I_{H_2S^+}$ against delay time t. Numbers on delay-curves refer to the nominal electron energy at which they were obtained.

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in fig. 6, curve 1. A good straight line is obtained with zero gradient, the intercept of which gives a value for the thermal rate constant, $k_1 = 2.76 \times 10^{-10}$ molecule⁻¹ cm³ sec⁻¹. At these low electron energies there is no contribution to the secondary ion formation by reaction (2).

In fig. 5 are plotted our delay curve data corresponding to eqn. (6) for a wide range of ion energies (19-48 eV). The slopes of these curves are given in table 2 and are



FIG. 6.—Curve 1, delay-curve slopes (fig. 4) against nominal electron energy; curve 2, delay-curve slopes (fig. 5) against I_{HS^+}/I_{H2S^+} . Abscissa for curve 1 given on upper scale.

plotted as a function of $I_{\text{HS}^+}/I_{\text{H}_2\text{S}^+}$ in fig. 6, curve 2, when a reasonable straight line is obtained, the gradient of which corresponds to k_2 and the intercept to k_1 . Leastsquares analysis of the data yield $k_1 = 2.76 \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ and $k_2 = 3.59 \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ sec}^{-1}$. The value for k_1 obtained by this plotting method is in complete agreement with the value of k_1 obtained by the pulsed-study at low electron energies.

ENERGY DEPENDENCE OF k_1 AND k_2

For ion-molecule reactions in which the interaction can be attributed to ioninduced dipole forces, Gioumousis and Stevenson¹⁷ have shown that the rate constant should be independent of ion energy so that the rate constants measured at 10.5 V cm^{-1} and under zero-field conditions should be the same. From table 1 (column 5) for hydrogen sulphide and several other comparable substrates the ratio $k_{\text{thermal}}/k_{10.5 \text{ V/cm}}$ is not unity. For reactions (1) and (2) the ratio is about 1.3, i.e., the rate constant is greater for the thermal energy ion. This is the reverse of the behaviour observed in the water system ¹ where the ratio is 0.82 for the reaction

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH.$$

Considering the errors involved in such work, these ratios are not significantly different from unity, which suggests that most of these reactions are in approximate agreement with the ion-induced dipole model in this energy range. In column 6 of table 1 we have calculated rate constants for the reactions on the basis of the ion-induced dipole model using the relation $k = 2\pi e(\alpha/\mu)^{\frac{1}{2}}$ where *e* is the electronic

charge, α is the polarizability of the neutral species and μ is the reduced mass of the colliding pair.

The experimentally measured values for the rate constants are much lower than the values calculated from the ion-induced dipole model; this difference may reflect the possibility that other reaction channels such as charge exchange are available to the collision complex. Also, such calculations do not include any consideration of ion-permanent dipole interactions. In this respect the dipole moment of hydrogen sulphide (0.93D) is much less than those of water (1.84D) or of ammonia (1.44D) and the rate constants for the hydrogen sulphide system are appreciably less than those for water or ammonia though the correlation may be fortuitous.

Although the ratio $k_{\text{thermal}}/k_{10.5 \text{ V/cm}}$ for reactions (1) and (2) is somewhat energy dependent, the ratio k_1/k_2 is not, having values of 0.77 under zero-field conditions, and 0.79 at 10.5 V cm⁻¹. Similar conclusions may be drawn from the data on the water and ammonia systems.

ION-MOLECULE REACTIONS INVOLVING H₂S

Mixtures of $argon+H_2S$, carbon monoxide+H₂S and carbon dioxide+H₂S were studied with the aim of investigating the thermochemically-possible reactions:

$A^+ + H_2S \rightarrow AH^+ + SH$,	$\Delta H \ ca. \ -13 \ kcal/mole^{-1}$
$\rm CO^+ + H_2S \rightarrow HCO^+ + SH$,	$\Delta H \ ca55 \ kcal/mole^{-1}$
$\text{CO}_2^+ + \text{H}_2\text{S} \rightarrow \text{HCO}_2^+ + \text{SH},$	$\Delta H \ ca. \ -29 \ kcal/mole^{-1}$

No evidence was found to indicate the formation of any of these secondary ions and it is concluded that, under our experimental conditions, the rate constants for the above reactions are zero or close to zero.

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