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CHEMICAL KINETICS IN THE GAS PHASE
PULSE RADIOLYSIS OF HYDROGEN SULFIDE SYSTEMS

Ole John Nielsen

Abstract. Formations and decays of HS and HS_2 radicals in the gas phase pulse radiolysis of pure H_2S, H_2S/Ar and H_2S/H_2 systems have been followed directly by kinetic spectroscopy. The literature on the subject is reviewed and a complete reaction scheme is discussed. Computer-simulations have been used to check the validity of the proposed mechanisms. Rate constants $k_{HS+HS} = (2.0 \pm 0.4) \times 10^{10}\ M^{-1}s^{-1}$ and $k_{H+H_2S} = (6.0 \pm 1.2) \times 10^{8}\ M^{-1}s^{-1}$ have been determined. The reaction of HS radicals with S atoms is responsible for the HS_2 formation. Pseudo-first order rate constants for reactions of HS with 1.3 butadiene, ethylene and molecular oxygen are reported.

INIS descriptors. ABSORPTION SPECTROSCOPY, CHEMICAL REACTION KINETICS, EXPERIMENTAL DATA, GASES, HYDROGEN SULFIDES, PULSED IRRADIATION, RADIATION CHEMISTRY, RADIOLYSIS, REVIEWS, SIMULATION.

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PREFACE

This report presents some of the work done by the author during his first year at Risø National Laboratory. The author has t ıed to make this report short and easily comprehensible.

All of the work has been carried out at the Accelerator, Chemistry and Computer Department of Risø National Laboratory guided by civ.ing. Palle Pagsberg. The author wishes to thank him for his great support and interest in the work.

The author owes great thanks to all the staff at the Chemistry Department Risø for creating such a stimulating environment, furthermore he thanks Risø for supplying the facilities and for financial support.

1. INTRODUCTION

When a material is subjected to high energy radiation (e.g. α-particles, γ-radiation or fast electrons), the primary products are electrons, positive ions and exited atoms and/or molecules. Interaction (e.g. relaxation, combination and decomposition) among these primary products may produce radicals, atoms and molecules, which in turn react to give final stable products.

Pulse radiolysis (irradiations by a short pulse of fast electrons) combined with some kind of transient detection method yields information about the kinetics of different chemical systems. The information obtained by pulse radiolysis is useful in many areas, supplementary and often complementary to information obtainable by other techniques. Recently the pulse radiolysis studies of gases have been excellently reviewed by Sauer (1976).

Only four gas phase pulse radiolysis studies on hydrogen sulfide systems are reported in literature (Willis et al., 1971a; Willis et al., 1971b; Boyd et al., 1973; Perner and Franken, 1969). In three of these studies (Willis et al., 1971a; Willis et al., 1971b; Boyd et al., 1973) the hydrogen yield, absolute dosimetry and the effect of SF_6 and sulfur as electron scavengers in the primary ionic processes were investigated. Only one gas phase pulse radiolysis study (Perner and Franken, 1969) has dealt with the kinetics of the non-ionic secondary reactions involving radicals, atoms and molecules. The transient species HS, HS_2 and S_2 were monitored by kinetic UV/VIS-spectroscopy and rate constants of reaction I and II were evaluated

(I) $HS + HS \rightarrow$ products; $k_I = 3.2 \times 10^{10}\ M^{-1}s^{-1}$

(II) $H + H_2S \rightarrow H_2 + HS$; $k_{II} = 7.7 \times 10^{8}\ M^{-1}s^{-1}$

Determining k_I involves the usual problem of estimating the initial concentration of HS-radicals just after the pulse. As the extinction coefficient for the observed HS-absorptionband is unknown, Perner and Franken's solution of this problem depends on the $G(H_2)$ value, where G is the number of molecules produced per 100 eV energy absorbed. Their $G(H_2)$ value was obtained by assuming a special distribution of the H_2 yield on specified reactions and on the basis of $G(N_2) = 10.0$ in N_2O. However, the fact that 12.4 seems to be the correct $G(N_2)$ value in case of Febetron dose rates (Willis et al., 1968; Willis et al., 1971a) suggests that $G(H_2)$ should have been increased. With these dubious assumptions the obtained value of $k_I = (3.2 \pm 0.3) \times 10^{10}\ M^{-1}s^{-1}$ is probably not very reliable. Perner and Franken (1969) also investigated H_2S/Ar and H_2S/Xe mixtures. As no complete reaction scheme was set up I have made a more exhaustive and hopefully more elucidating investigation including experiments on pure H_2S, H_2S/Ar, H_2S/He, H_2S/H_2 mixtures and experiments with electron and radical scavengers.

All reactants and reaction products needed to be considered in all reported experiments are listed in table 1 together with the heat of formation, $H^o_{f\ 298}$. The values of $H^o_{f\ 298}$ are taken from Benzon (1978) and references therein.

Table 1. $H^o_{f\ 298}$ in kcal/mole for the considered reactants and products

H	52.1
H_2S	-4.9
HS	35
H_2S_2	3.8
S	66.3
S_2	30.7
HS_2	22.1
H_2	0
S_4	31
HS_3	25.3
H_2S_3	7.4
H_2S_4	10.6

To be sure to consider all imaginable reactions the quadratic array in fig. 1 is set up. In table 2 all these reactions are listed with the standard enthalpy change. The numbering from table 2 is used throughout this report.

Table 2. Considered reactions and the standard enthalpy change in kcal/mole

(11)	$H + H$	$\rightarrow$	H_2	-104.2
(12)	$H + H_2S$	$\rightarrow$	$H_2 + HS$	- 12.3
(13a)	$H + HS + M$	$\rightarrow$	H_2S	- 92.0
(13b)	$H + HS$	$\rightarrow$	$H_2 + S$	- 20.8
(14a)	$H + H_2S_2$	$\rightarrow$	$H_2 + HS_2$	- 33.8
(14b)		$\rightarrow$	$HS + H_2S$	- 25.8
(15)	$H + S + M$	$\rightarrow$	HS	- 83.4
(16a)	$H + S_2 + M$	$\rightarrow$	HS_2	- 60.7
(16b)	$H + S_2$	$\rightarrow$	$HS + S$	+ 18.5
(17a)	$H + HS_2 + M$	$\rightarrow$	H_2S_2	- 70.4
(17b)	$H + HS_2$	$\rightarrow$	$H_2 + S_2$	- 43.5
(17c)		$\rightarrow$	$HS + HS$	- 4.2
(23a)	$H_2S + HS$	$\rightarrow$	$H_2 + HS_2$	- 8.0
(23b)		$\rightarrow$	$H_2 + H + S_2$	+ 52.7
(25a)	$H_2S + S + M$	$\rightarrow$	H_2S_2	- 57.6
(25b)	$H_2S + S$	$\rightarrow$	$H_2 + S_2$	- 30.7
(25c)		$\rightarrow$	$HS + HS$	+ 8.6
(25d)		$\rightarrow$	$H + HS_2$	+ 12.8
(26)	$H_2S + S_2$	$\rightarrow$	?	
(27)	$H_2S + HS_2$	$\rightarrow$	?	
(28)	$H_2S + H_2$	$\rightarrow$	?	
(33a)	$HS + HS + M$	$\rightarrow$	H_2S_2	- 66.2
(33b)	$HS + HS$	$\rightarrow$	$H_2S + S$	- 8.6
(33c)		$\rightarrow$	$H_2 + S_2$	- 39.3
(33d)		$\rightarrow$	$H + HS_2$	+ 4.2
(34)	$HS + H_2S_2$	$\rightarrow$	$H_2S + HS_2$	- 21.6
(35a)	$HS + S + M$	$\rightarrow$	HS_2	- 79.2
(35b)	$HS + S$	$\rightarrow$	$H + S_2$	- 18.5

cont.

(36a)	$HS + S_2 + M \rightarrow$	HS_3	- 40.4
(36b)	$HS + S_2 \rightarrow$	$HS_2 + S$	+ 22.7
(37a)	$HS + HS_2 \rightarrow$	$H_2S + S_2$	- 31.3
(37b)	$HS + HS_2 \rightarrow$	$H_2S_2 + S$	+ 13.0
(38)	$HS + H_2 \rightarrow$	$H_2S + H$	+ 12.2
(45a)	$H_2S_2 + S + M \rightarrow$	H_2S_2	- 62.7
(45b)	$H_2S_2 + S \rightarrow$	$HS + HS_2$	- 13.0
(45c)	$\rightarrow$	$S_2 + H_2S$	- 44.3
(55)	$S + S + M \rightarrow$	S_2	-101.9
(56)	$S + S_2 + M \rightarrow$	$c\text{-}S_3$	- 64.5
(57)	$S + HS_2 + M \rightarrow$	HS_3	- 63.1
(58)	$S + H_2 + M \rightarrow$	H_2S	- 71.2
(66)	$S_2 + S_2 + M \rightarrow$	$c\text{-}S_4$	- 30.4
(67)	$S_2 + HS_2 + M \rightarrow$	HS_4	
(77a)	$HS_2 + HS_2 + M \rightarrow$	H_2S_4	- 33.6
(77b)	$HS + HS_2 + M \rightarrow$	$H_2S_2 + S_2$	- 9.7
(77c)	$\rightarrow$	$H_2 + S_2 + S_2$	+ 17.2
(78)	$HS_2 + H_2 \rightarrow$	$H_2S_2 + H$	+ 33.8

2. EXPERIMENTAL

The gas samples were irradiated with 2 MeV electrons from a Febetron 705 B field emission accelerator with a pulse duration of 30 nsec and a maximum current of 3000 Amp. The gas mixtures were prepared on a conventional all-glass vacuum line and transferred to a 1 liter stainless steel cell adopted from Gordon et al. (1971) equipped with a set of conjugate mirrors as described by White (1942). This arrangement allows multiple passes of the analyzing light beam through the sample cell. Most experiments were carried out using twelve traversals corresponding to an optical path length of 120 cm. A Varian 150 W high-pressure Xenon lamp with aluminized parabolic reflector and sapphire window provided an analyzing light beam of high brightness in the ultraviolet region. A Hilger and Watts 1 meter

grating spectrometer was used with a 1200 grooves/mm grating blazed at 3000 Å to obtain high efficiency in the spectral range of interest and a reciprocal dispersion of 8 Å/mm. The light intensity passing the exit slit was monitored using a Hamamatsu R928 photomultiplier coupled to a current input operational amplifier with adjustable off-set representing 100% light transmission. The transient signals were sampled and digitized in a transit recorder and transferred to a minicomputer. Here the raw-data may be transformed into absorbance versus time curves or other relevant plot types under control from a teletype. Simple first and second order plots can be inspected on a display screen and plotted on a X-Y recorder. Selected raw-data are stored on magnetic tape for further processing on a large central computer where complex kinetic curves can be compared with simulated models. The experimental set-up is shown in figs. 2 and 3 and described in detail by Hansen et al. (1979).

Dosimetry was performed by monitoring the formation of ozone in 1 atm of oxygen. The in situ measurement of ozone offers an advantage for systems where the electron beam flux and the dose distribution are non-uniform. The average O_3 absorbance at 2550 Å, measured with an optical path length of 120 cm and a band pass of 8 Å, was 0.626. Using $G(O_3) = 12.8$ (Willis and Boyd, 1976) and the extinction coefficient $\varepsilon(O_s) = 3067\ M^{-1}cm^{-1}$ determined by Inn and Tanaka (1953) we calculate a maximum dose off 116 krad per irradiation pulse corresponding to the unattenuated electron beam. Assuming a stopping power of H_2S equal to that of O_2 the doses in all mixtures can be calculated using the relative stopping powers quoted by Willis et al. (1968), and Baily and Brown (1959). The irradiation doses could be varied using stainless steel diaphragms as electron beam attenuators.

Care has been taken to check the applicability of the Lambert-Beer law $A = \varepsilon \cdot l \cdot c$, where A is the absorbance, ε the extinction coefficient, l the optical path length and c is the concentration. When the used band-pass is wider than the spectral features of the transient absorption bands one has to work with a modified version of the Lambert-Beer relation, $A = (\varepsilon \cdot l \cdot c)^n$.

Here n is a fractional power. Applicability of this relation has been investigated in detail by Bourene et al. (1974). The value of n depends on the line shape and the spectrometer slit setting and must be determined experimentally.

Because of the rather complex reaction system we found it necessary to make use of simulated kinetic models in order to evaluate the absolute rate constants for the most significant reactions involved. A computerprogram, CHEMSIMUL, developed by Ole Lang Rasmussen (1978) was applied. As input, this program accepts reaction shemes in the usual chemical notation, viz.,

$$H + H_2S \rightarrow H_2 + HS; \quad k = 7.7 \times 10^8\ M^{-1}s^{-1}$$

etc.

The program translates the "chemical equations" into a pertinent set of differential equations which is solved by numerical integration after specification of initial conditions, G-values and irradiation dose. The effect of parameter variation can be studied by a semi-interactive procedure using a graphical computer terminal.

Formations and decays of HS, HS_2 and S_2 were studied by monitoring absorption bands at the following wavelengths:

HS : 3240 Å; Q_1-branch - 0,0 transition in the $A^2\Sigma^+ - X^2\Pi$ band

S_2 : 2829 Å; 9.0 transition in the $B^3\Sigma_u^- - X^3\Sigma_y^-$ band

HS_2: 3408 Å and 3483 Å; in the $A^2A' - X^2A''$ band.

The value of n in the modified version of the Lambert-Beer relation has in each case been determined by plotting the logarithm of the maximum absorbance vs. the logarithm of the dose, using different doses.

3. RESULTS AND DISCUSSIONS

3.1. The pure H_2S-system

For the sake of completeness the primary ionic processes (also occuring in mixtures) should be mentioned here. From mass-spectrometric studies (Cornu and Massot, 1966) the predominant ions in the radiolysis of H_2S are H_2S^+(52%), HS^+(22%), S^+(23%) and H^+(3%) formed in reactions such as (III)-(VI):

(III) $H_2S \rightarrow H_2S^+ + e$
(IV) $\rightarrow HS^+ + H + e$
(V) $\rightarrow S^+ + + H + e$
(VI) $\rightarrow H^+ + HS + e$

further reactions can be (VII)-(IX):

(VII) $H_2S^+ + H_2S \rightarrow H_3S^+ + HS$
(VIII) $HS^+ + H_2S \rightarrow H_3S^+ + S$
(IX) $H^+ + H_2S + M \rightarrow H_3S^+ + M.$

The fate of sulfur is not clear. Neutralization processes can be (X)-(XIII):

(X) $H_3S^+ + e \rightarrow H + H_2S$
(XI) $\rightarrow H_2 + HS$
(XII) $\rightarrow H + H + HS$
(XIII) $S^+ + e \rightarrow S$.

The result of all these ionic and neutralisization processes can be described as (XIV)-(XVI):

(XIV) $H_2S \rightarrow H + HS$
(XV) $\rightarrow H_2 + S$
(XVI) $\rightarrow H + H + S$.

The relative importance of these reactions are unknown, but reaction (XV) must be very improbable. H atoms are removed

very rapidly in pure H_2S by reaction 12:

(12) $H + H_2S \rightarrow H_2 + HS$.

Therefore the only species present in the pure H_2S system 1 μsec after the pulse are H_2S, H_2, HS and S. H_2 will be present in an amount equal to [HS] + 1/2[S]. A few experiments on the pure H_2S system have been performed. HS absorption has been followed for 400 μsec in 760 and 380 torr pure H_2S and for 20 μsec in 760 torr H_2S. HS_2 absorption was followed for 400 μsec in 780 torr H_2S. Unfortunately the HS absorption in 380 and 760 torr H_2S were recorded with different slit widths, hence both ε, n and c_o (c_o is the start-concentration) are different in these two experiments. In figs. 4 and 5 the experimental curves are shown.

The absence of a typical "second order tail" in fig. 4 indicates contributions from one or more side reactions competing with the simple second order decay (33a-33c). The low residual absorption lasting for 400 μsec might be due to spectral overlab from another species. This possibility was cheched by monitoring the transient signals above and below the characteristics HS absorption.

A prompt continuous absorption amounts to approximately 10% of the HS maximum absorbance. Attempts to fit the experimental data (with and without subtraction of the constant absorbance) to simple first or second order kinetics, were unsuccessful. The decay of both HS and HS_2 must be of mixed order, predominantly second order.

The exothermic reactions given in table 3 may all contribute to the removal of HS in the pure H_sS-system. Reaction 23a has not been taken into account elsewhere, but will be considered here as a possible source of HS_2. Reactions 33 are definetely taking place since a second order "tail" is observed.

Table 3. HS removal reactions in the pure H_2S system

		ΔH kcal/mole
(13a)	$H + HS + M \rightarrow H_2S$	-92.0
(13b)	$H + HS \rightarrow H_2 + S$	-20.8
(23a)	$H_2S + HS \rightarrow H_2 + HS_2$	- 8.0
(23b)	$H_2S + HS \rightarrow H_2 + H + S_2$	+52.7
(33a)	$HS + HS + M \rightarrow H_2S_2$	-66.2
(33b)	$HS + HS \rightarrow H_2S + S$	- 8.6
(33c)	$HS + HS \rightarrow H_2 + S_2$	-39.3
(33d)	$HS + HS \rightarrow H + HS_2$	+ 4.2
(34)	$HS + H_2S_2 \rightarrow H_2S + HS_2$	-21.6
(35a)	$HS + S + M \rightarrow HS_2$	-79.2
(35b)	$HS + S \rightarrow H + S_2$	-18.5
(36a)	$HS + S_2 + M \rightarrow HS_3$	-40.4
(36b)	$HS + S_2 \rightarrow HS_2 + S$	+22.7
(37a)	$HS + HS_2 \rightarrow H_2S + S_2$	-31.3
(37b)	$HS + HS_2 \rightarrow H_2S_2 + S$	+13.0
(38)	$HS + H_2 \rightarrow H_2S + H$	+12.2

The reaction, HS + HS → products, can be described as proceeding through an activated intermediate, $H_2S_2^*$, which might be stabilised at large pressures or decompose:

(33a) $HS + HS \rightleftarrows H_2S_2^* \overset{M}{\rightleftarrows} H_2S_2$
(33b) $HS + HS \rightleftarrows H_2S_2^* \rightarrow H_2S + S$
(33c) $HS + HS \rightleftarrows H_2S_2^* \rightarrow H_2 + S_2$
(33d) $HS + HS \rightleftarrows H_2S_2^* \rightarrow H + HS_2$.

Reaction (33d) is endothermic and no evidence for this recombination route has been presented. In the work of Bradley et al. (1973) the value of k_{33b} was found to be $7.8 \times 10^9\ M^{-1}s^{-1}$. Perner and Franken (1969) assume that reaction (33c) is the dominating source of the S_2.

However, an alternative reaction (25), $H_2S + S \rightarrow$, might produce S_2 via another activated $H_2S_2^{**}$ intermediate. In the OH recombination the reaction analogous to 33b is dominating (Fair and Thrush, 1969). Determination of k_{33b} involves the problem of estimating the initial HS concentration. Assuming the G(HS) value equal to that of O_2, the initial HS concentration is calculated to be $c_o(HS) \approx 1.04 \times 18.6 \times 120 \times 10^{-9} = 2.3\ \mu M$. From the experimental decay half-lives the second order rate constant can be calculated $\tau = \frac{1}{c_o \cdot k} \Rightarrow k_{33b} \sim 2.0 \times 10^{10}\ M^{-1}s^{-1}$.

The higher value of k_{33b} obtained in this and the work of Perner and Franken (1969) compared to that of Bradley et al. (1973) suggests additional removal of HS by e.g. reaction 23a:

(23a) $HS + H_2S \rightarrow H_2 + HS_2$.

This reaction may also explain the fast appearance of HS_2 in our experiments. All potentional HS_2 source reactions are listed in table 4. If reaction 23a is the source reaction for HS_2 then $\tau(23a) = \ln 2/(k_{23a} \cdot [H_2S]_o)$, i.e. the formation half-life of HS_2 decreases with increasing concentration of H_2S. This possibility will be investigated in the mixed H_2S/Ar system. It has not been possible to explain the difference in HS_2 formation half-life in these and in the experiments of Perner and Franken (1969).

Tabel 4. HS_2 source reactions

(14a)	$H + H_2S_2$	$\rightarrow HS_2 + H_2$
(16a)	$H + S_2 + M$	$\rightarrow HS_2$
(23a)	$HS + H_2S$	$\rightarrow HS_2 + H_2$
(25d)	$H_2S + S$	$\rightarrow HS_2 + H$
(33d)	$HS + HS$	$\rightarrow HS_2 + H$
(34)	$HS + H_2S_2$	$\rightarrow HS_2 + H_2S$
(35a)	$HS + S + M$	$\rightarrow HS_2$
(36b)	$HS + S_2$	$\rightarrow HS_2 + S$
(45)	$H_2S_2 + S$	$\rightarrow HS_2 + HS$

If the k_{33b} value from Bradley et al. (1973) and the $c_o(HS)$ = 2.3 μM are assumed to be valid it is possible to find a value of k_{23a} reproducing the experimental HS decay and HS_2 formation. A computer simulation taking $k_{23a} = 5 \times 10^5\ M^{-1}s^{-1}$ gives HS half-life 18 μsec, which is in good agreement with the experimental value of approximately 17 μsec.

Since S atoms undoubtly are among the primary products it is seen from table 4 that reaction 35a, which is 10 times more exothermic than reaction 23a, should be considered as a possible HS_2 source reaction. Besides reaction 35a there will be two other competitive sulfur consuming reactions:

(35b) $HS + S \rightarrow H + S_2$
(55) $S + S \overset{M}{\rightarrow} S_2$.

There has been only one determination of k_{35b} by Mihelcic and Schindler (1970), who found the value of k_{35b} to be approximately $3 \times 10^{10}\ M^{-1}s^{-1}$. The gas-phase recombination reaction (55) of sulfur atoms is not well understood and there is a large scatter in the published values of the rate constant k_{55}. The reported values of k_{55} lie in the range $10^{12} \times [M]$ to $10^{15} \times [M]$ (Howgate and Barr, 1973; Basco and Pearson, 1967), where [M] is the concentration of third bodies.

The only two reactions considered responsible for the HS_2 removal are reaction 37 and 77. k_{37} has to be greater than $10^{11}\ M^{-1}s^{-1}$ to reproduce the HS_2 decay. This value seems unrealistic. Taking $k_{77} = 2 \times 10^{10}\ M^{-1}s^{-1}$ the HS_2 decay are reproduced satisfactorily.

The experimental data on the pure H_2S system are too few to establish a unique complete kinetic model.

Perner and Franken (1969) proposed another HS_2 formation mechanism:

(33b) $HS + HS \rightarrow H_2S + S$ $7.8 \times 10^9\ M^{-1}s^{-1}$

(33a) $HS + HS \overset{M}{\rightleftharpoons} H_2S_2$?

(34) $HS + H_2S_2 \rightarrow HS_2 + H_2S$ $2 \times 10^7\ M^{-1}s^{-1}$,

where k_{34} is determined in the work of Perner and Franken (1969). No value of k_{33a} can reproduce the HS_2 formation observed experimentally.

3.2. The H_2S/Ar system

In pulse radiolysis of H_2S/Ar mixtures, energy will be absorbed by H_2S and Ar according to relative stopping powers and relative concentrations. Rare gas sensitized radiolysis of H_2S has been investigated in detail (Jowko et al., 1977; Foryś et al., 1976; Ahmad et al., 1972; Jezierska and Foryś, 1972; Jezierska, 1971). As in the pure H_2S system the result of the primary reactions will be:

(XIV) $H_2S \rightarrow H + HS$

(XV) $\rightarrow H_2 + S$

(XVI) $\rightarrow H + H + S$.

Since no molecular hydrogen was observed among the primary products in the experiments of Jezierska and Foryś (1972) the very improbable reaction XV is neglected.

Compared to the pure H_2S case reaction 12:

(12) $H + H_2S \rightarrow H_2 + HS$,

will remove H atoms and produce HS radicals more slowly because of the smaller H_2S concentration. In fig 6 is shown the variation of HS absorbance in the first 40 μsec after the pulse in 2 torr H_2S with Ar to 1 atm.

If HS removal is neglected the HS formation should consist of a prompt component from reaction XIV and a slower rising component from reaction 12 (see fig. 7). This is exactly what is seen in fig. 6.

In fig. 8 some typical observed maximum HS absorbances are plotted for different partial pressures of H_2S backed up with Ar to 1 atm. The increasing HS yield with higher H_2S partial pressures should cause HS to be removed faster by reaction 33b,

(33b) $HS + HS \rightarrow H_2S + S$,

which is definitely taking place. This assumption is in good agreement with the experimental data.

One of the main problems is to determine the relative importance of reaction XIV and XVI. To find a compound scavenging only H atoms and not HS radicals would be a convenient aid in solving this problem. However, in all experiments with H_2S partial pressures from 1 to 10 torr the ratio between the slower and the prompt rising component of the HS absorbance seems to be constant, around 1:2.

From the complete reaction scheme (table 2) it seems necessary to consider the following reactions:

(11) $H + H \overset{M}{\rightleftharpoons} H_2$

(12) $H + H_2S \rightarrow H_2 + HS$

(13) $H + HS \rightarrow$ products

(15) $H + S \overset{M}{\rightleftharpoons} HS$

(23) $H_2S + HS \rightarrow$ products

(25) $H_2S + S \rightarrow$ products

(33) $HS + HS \rightarrow$ products

(35) $HS + S \rightarrow$ products

(55) $S + S \overset{M}{\rightleftharpoons} S_2$.

Reaction 23a and 35a have been proposed as HS_2 source reactions:

(23a) $H_2S + HS \rightarrow HS_2 + H_2$

(35a) $HS + S \overset{M}{\rightarrow} HS_2$.

The observed HS_2 maximum absorbance for different H_2S partial pressures is plotted in fig. 9. Experimentally it is found that the rate of formation and the yield of HS_2 are independent of the H_2S partial pressures. Likewise, the half-life of the HS decay remains independent of $[H_2S]_o$. On this basis it is concluded that reaction 23a contributes only to a minor extent, if at all, to the formation of HS_2.

3.3. The H_2S/H_2-system

No pulse radiolysis studies of H_2S/H_2 mixtures have been reported in literature.

Here, as in the H_2S/Ar-system, the energy will be absorbed by H_2S and H_2 according to their relative stopping powers and relative concentrations. Assuming stopping power to be proportional to density, the relative stopping powers of H_2 and H_2S will be 2 to 34. For partial pressures of H_2S less than 25 torr and H_2 to 1 atm, more than 75% of the energy will then be absorbed by H_2 and the primary consequence is:

$$H_2 \rightarrow H + H .$$

3.3.1. Formation of HS

The produced H-atoms will be removed by reaction 12 to produce H_2 molecules and HS radicals:

(12) $H + H_2S \rightarrow H_2 + HS$.

HS-radical absorbance has been observed after radiation of mixtures of 0.1 to 100 torr H_2S with H_2 to 1 atm. Observation-

time-intervals ranged from 20 to 400 μsec. Two sets of experements using different slit widths were carried out. In fig. 10 is shown recorded HS-absorbance in the first 40 μsec after the pulse in 5 torr H_2S with H_2 to 1 atm. All experimental data are given in tables 5 and 6.

Table 5. Experimental data from the H_2S/H_2-system

$p(H_2S)$ in torr	$100 \times A_{max}$	decay half-life in μsec.	$10^5 \times 1/(\tau_d \cdot A_m)$
5	3.31	63	4.8
5	3.73	83	3.3
10	4.79	64	3.1
10	4.78	70	2.9
15	3.51	60	4.7
15	4.25	64	3.7
20	4.57	63	3.5
20	4.49	64	3.5
25	5.04	56	3.6
25	5.07	64	3.8
50	5.09	57	3.4
50	5.51	58	3.1
100	7.17	45	3.1
100	5.96	50	3.3

Table 6. Experimental data from the H_2S/H_2-system

$p(H_2S)$ in torr	$100 \times A_{max}$	formation half-life in μsec.	$10^9 \times \ln 2/(\tau_f \cdot c_o)$
0.5	2.2	13.5	1.87
0.5	1.9	14.0	1.80
1.0	2.6	6.2	2.00
1.0	2.3	6.5	1.95
2.0	2.7	5.5	1.15
2.0	2.8	5.6	1.13
3.0	2.8	5.0	0.84
3.0	2.6	4.2	1.00
4.0	3.4	4.2	0.75
4.0	3.3	3.8	0.83
5.0	3.0	3.4	0.74
10.0	3.5	2.0	0.63
25.0	3.9	1.4	0.36

Assuming reaction 12 to follow simple pseudo-first order kinetics the rate constant k_{12} can be determined as $k_{12} = \ln 2/(\tau_f \cdot c_o)$, where τ_f is the HS formation half-life and c_o, the initial H_2S concentration. k_{12}-values calculated this way from 13 experiments with H_2S concentrations ranging from 0.5 to 50 torr are also given in table 6 and plotted in fig. 11. If the simple pseudo-first order assumption was valid the calculated k_{12}-values should be independent of the initial H_2S concentration. The too high values of k_{12} above the dotted line in fig. 11 are significant proof that other H and HS loss reactions have to be considered. These additional reaction are:

(11) $H + H \overset{M}{\rightarrow} H_2$

(13a) $H + HS \overset{M}{\rightarrow} H_2S$

(13b) $H + HS \rightarrow H_2 + S$

(33a) $HS + HS \overset{M}{\rightarrow} H_2S_2$

(33b) $HS + HS \rightarrow H_2S + S$

(33c) $HS + HS \rightarrow H_2 + S_2$.

The derived "asymptotic" k_{12}-value of 2×10^8 $M^{-1}s^{-1}$ is in fair agreement with the value of 4.35×10^8 $M^{-1}s^{-1}$ found by Kurylo et al. (1971).

To establish a consistent model for the HS-formation and decay, reactions 11, 12, 13a, 13b, 33a, 33b and 33c should be considered.

There have been nummerous investigations of reaction 11 involving different third bodies and $k_{11} = 3 \times 10^{12}$ $M^{-1}s^{-1}$ with H_2 as third body (Larkin and Thrush, 1964; Ham et al., 1970) seems to be the most reliable value.

No experimental data on reaction 13a are reported in literature. $k_{13b} = 1.5 \times 10^{10}$ $M^{-1}s^{-1}$ has been found from discharge flow studies (Bradley et al., 1973).

As seen from table 2 there are three possible exothermic HS recombination reactions. It has been shown that of reactions 33b and 33c, reaction 33b predominates, especially at lower pressures (Forbes et al., 1938; Darwent, 1953; Darwent and Roberts, 1953). This is quite analogous to OH recombination Fair and Thrush, 1969). It is not possible to presume anything about the importance of reaction 33a.

To simulate the HS formation and removal it is necessary to include reactions 11, 12, 13b, and 33, where reaction 33 is HS + HS → products. The two uncertain parameters in this model are k_{33} and G(H).

Unknowns are determined using a normal simpel iterative trial and error method.

G(H) was found to be approximately 12 and k_{12} to be 6×10^8 $M^{-1}s^{-1}$ rather than 4.3×10^8 $M^{-1}s^{-1}$. Model HS concentration variation was not very sensitive to changes in k_{33}. From the computer simulations it can be seen that k_{33} must have a value in the range $7\text{-}20 \times 10^{10}$ $M^{-1}s^{-1}$.

The deviations from simple pseudo-first order kinetics (see fig. 11) is caused by additional H and HS loss reactions taking place. Reaction 11 has been shown to be unimportant as expected. Computer simulations show that reaction 12 becomes pseudo-first order for H_2S partial pressures above 3 torr. Reaction 13b is expected to be of importance for small H_2S partial pressures when both H and HS are present in about equal concentrations at the same time. Reaction 33 is expected to be important also at higher H_2S partial pressures. k_{12} values from a theoretical model including reactions 11, 12, 13 and 33 are plotted and compared with the experimentally derived values in fig. 11. The agreement is quite good.

3.3.2. Decay kinetics

If reaction 33, HS + HS → products, is assumed to be the only HS consuming reaction, then $2 \times k_{33}/(\varepsilon \cdot \ell)$ is equal to $1/(\tau_d \cdot A_m)$, where τ_d is the observed HS decay half-life and A_m the observed HS maximum absorbance. The average value of $1/(\tau_d \cdot A_m)$ from 14 experiments tabulated in table 5 is $3.56 \times 10^5\ s^{-1}$. An accurate value of k_{33} can not be calculated until the extinction coefficient ε of the HS radical has been accurately determined. But estimating ε to be around $10^3\ M^{-1}cm^{-1}$ and using the applied optical path length $l = 120$ cm, k_{33} is estimated to be approximately $2 \times 10^{10}\ M^{-1}s^{-1}$. This value is in good agreement with the value of $8 \times 10^9\ M^{-1}s^{-1}$ estimated from the present computer simulations and the value $7.8 \times 10^9\ M^{-1}s^{-1}$ determined by Bradley et al. (1973).

3.3.3. Significance of the absence of HS_2 in the H_2S/H_2 system

No formation of HS_2 was observed in experiments with H_2S/H_2 mixtures. This could be due to insufficient contemporary HS and S concentrations to yield HS_2 via the formation reaction proposed in this work:

(35a) $\quad HS + S \overset{M}{\rightleftharpoons} HS_2$.

Deactivation efficiency towards possibly produced H_2S_2 is expected to decrease from H_2S through H_2 to Ar as third bodies. HS_2 is observed in experiments both in pure H_2S and in H_2S/Ar mixtures. Therefore, misssing HS_2 in H_2S/H_2 mixtures can not be explained by different deactivation efficiency of H_2 towards H_2S_2, but must be due to insufficient contemporary HS and S concentrations.

4. REACTIVITY OF THE HS-RADICAL WITH ADDED SUBSTRATES

The reactivity of the HS-radical towards 1,3-butadiene, ethylene and oxygen hasbeen investigated. By adding small amounts of the compound in question to the H_2S/Ar system the HS-decay is changed to be of pure first order. From the measured HS decay half-lives the corresponding rate constants are estimated. These are shown and compared with those of Perner and Franken (1969) in table 7. The rate constants obtained in the present work seem to be in agreement with those reported by Perner and Franken.

Table 7. Rate constants for HS-radical reactions in $M^{-1}s^{-1}$

HS + reactant	This work	Perner and Franken
HS	8×10^9	3.2×10^{10}
1,3-butadiene	3.8×10^{10}	6.0×10^{10}
1,4-cyclohexadiene		7.3×10^9
allene		8.3×10^7
ethylene	8×10^7	
vinylchloride		7.4×10^7
cyclohexene		4.7×10^7
H_2S_2		2×10^7
benzene		8×10^6
O_2	$<5 \times 10^6$	

5. THE FUTURE

More reliable values for the second order rate constants can only be derived when the HS concentration is known more accurately. This is possible when the extinction coefficient for the observed HS absorption band is known. This quantity can be determined from experiments on H_2S/H_2 mixtures if the G(H) value in pure H_2 was known. It is very surprising that nobody has ever determined this important quantity. We intend to determine G(H) in H_2 by irradiating H_2 containing small amounts of HI and measuring the yield of I_2.

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	H	H_2S	HS	H_2S_2	S	S_2	HS_2	H_2
H	11	12	13	14	15	16	17	-
H_2S		-	23	-	25	-	-	-
HS			33	34	35	36	37	38
H_2S_2				-	45	-	-	-
S					55	56	57	58
S_2						66	67	-
HS_2							77	78
H_2								-

Fig. 1. Kvadratic array showing the reactions considered and their numbering used throughout this report.

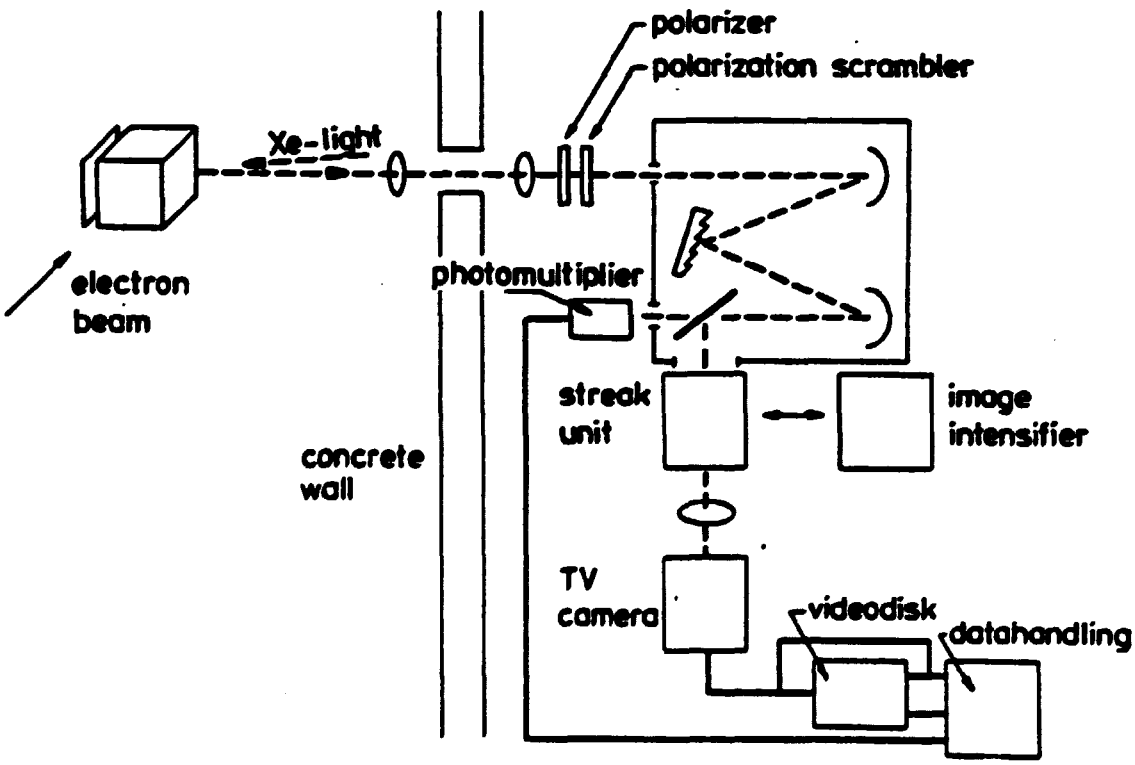

Fig. 2. Experimental setup.

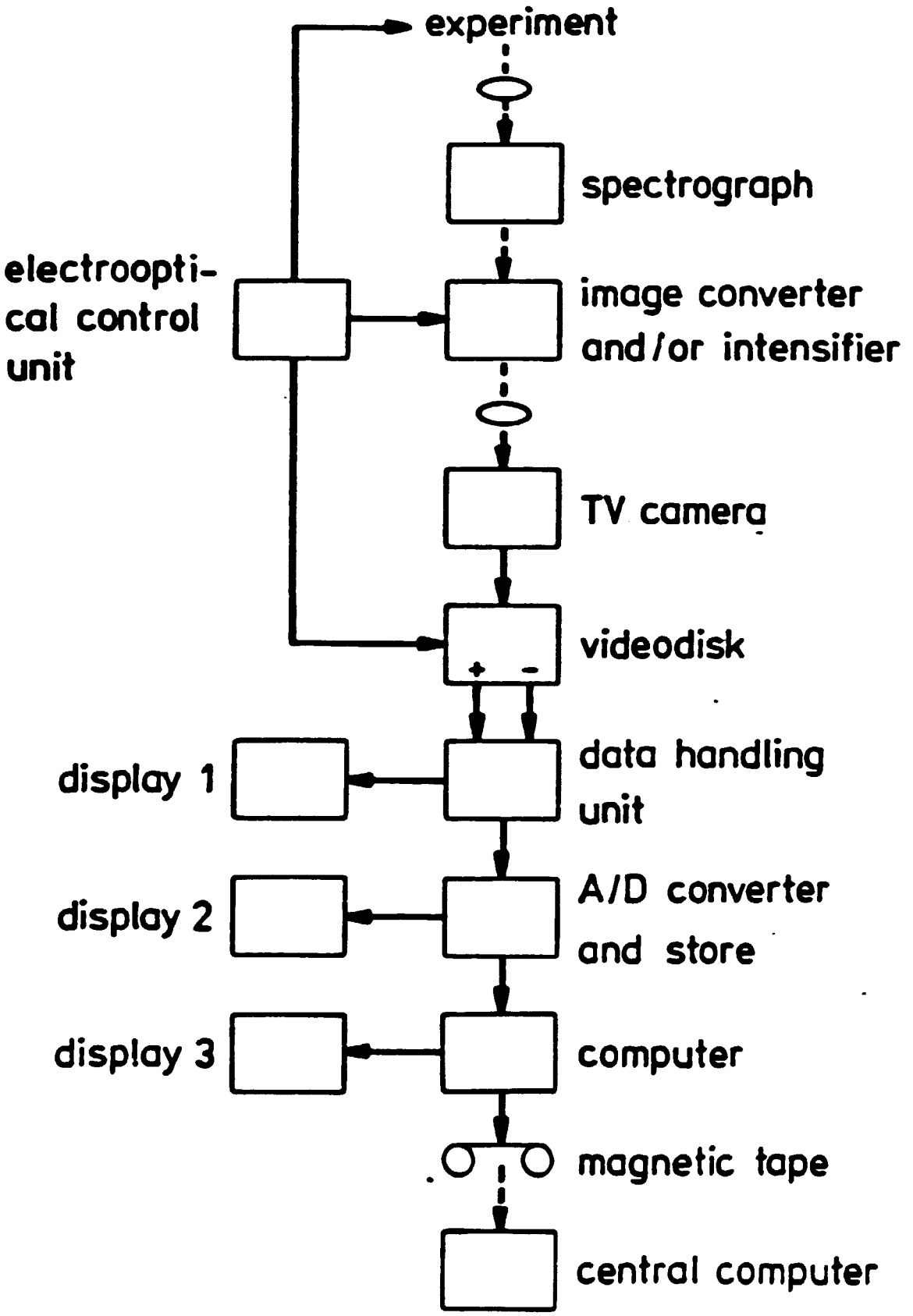

Fig. 3. Block diagram of the detection system.

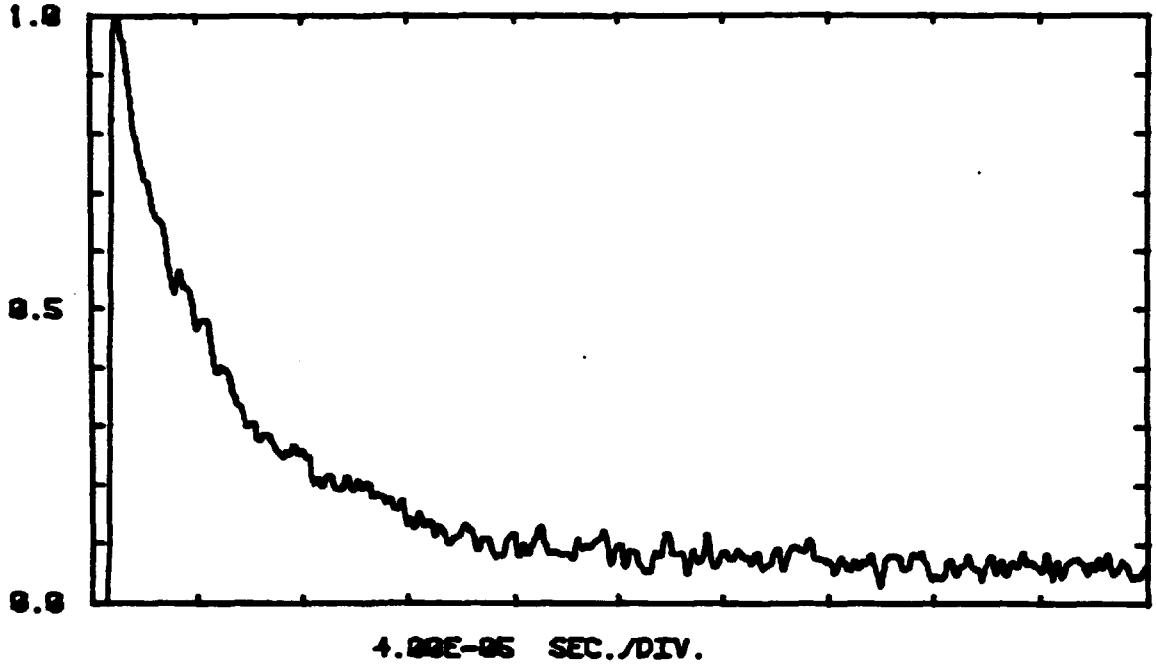

Fig. 4. Experimental HS decay in 760 torr pure H_2S monitored at 3241 Å. T = 295 ± 1 K.

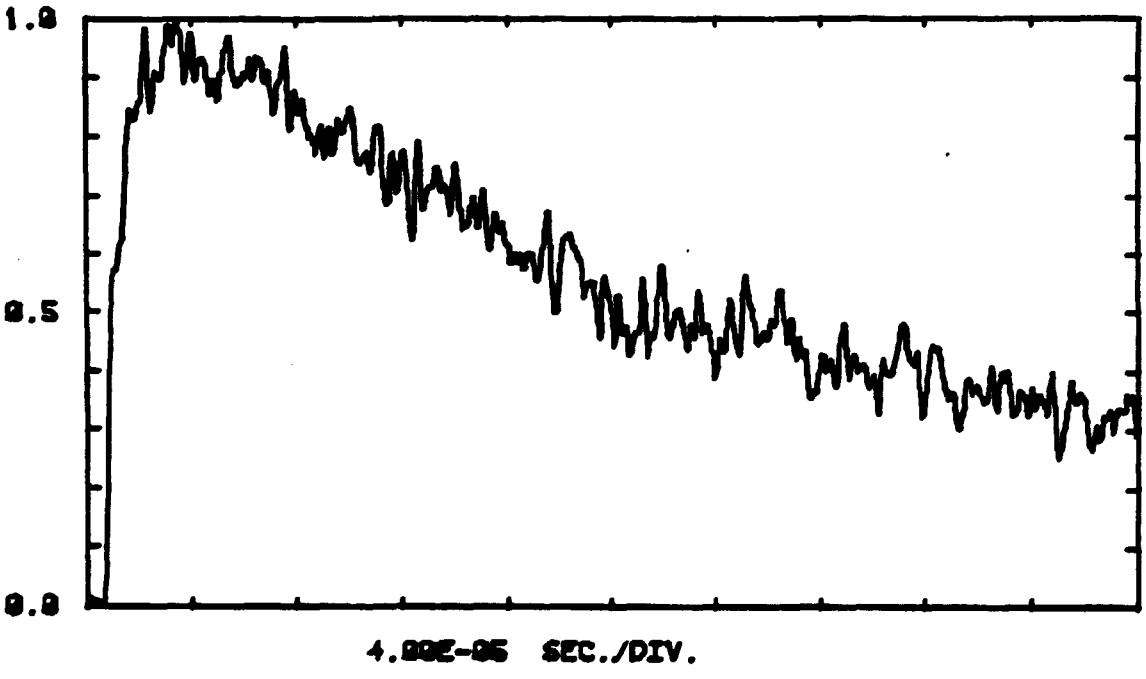

Fig. 5. Experimental HS_2 formation and decay in 760 torr pure H_2S monitored at 3448 Å. T = 295 ± 1 K.

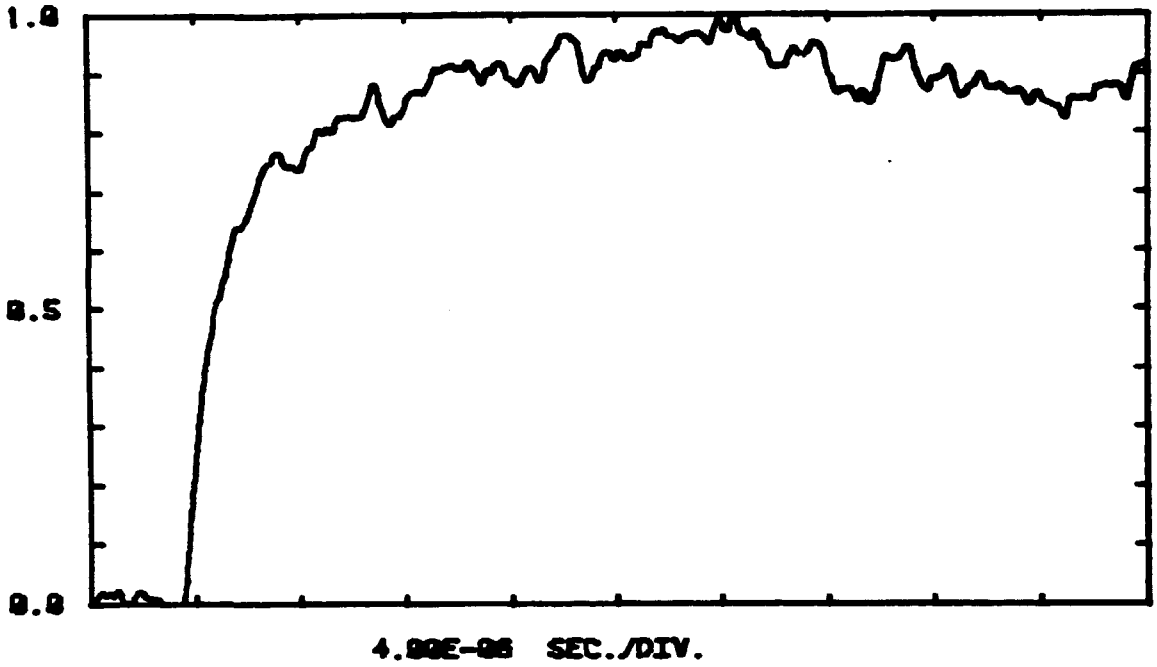

Fig. 6. Experimental HS formation in 2 torr H_2S with Ar to 760 torr. Monitored at 3241 Å. T = 295 ± 1 K.

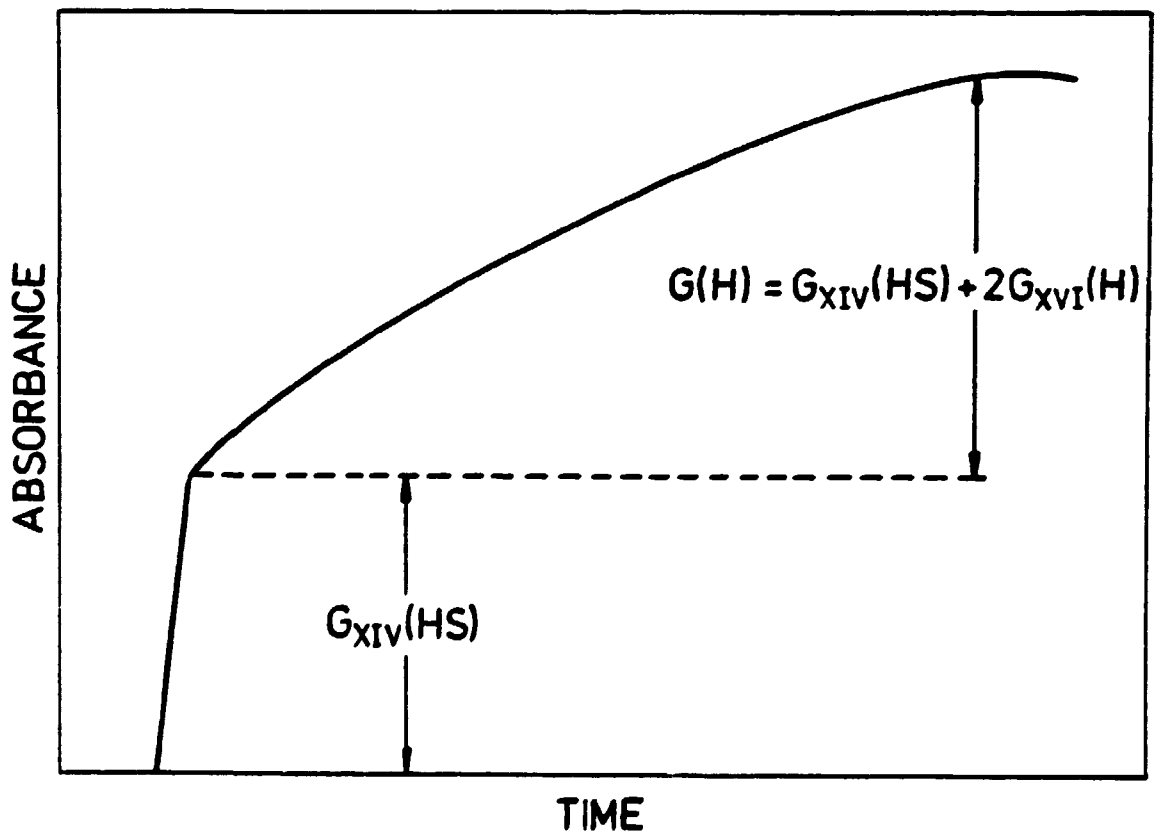

Fig. 7. Theoretically predicted HS formation in H_2S/Ar mixtures.

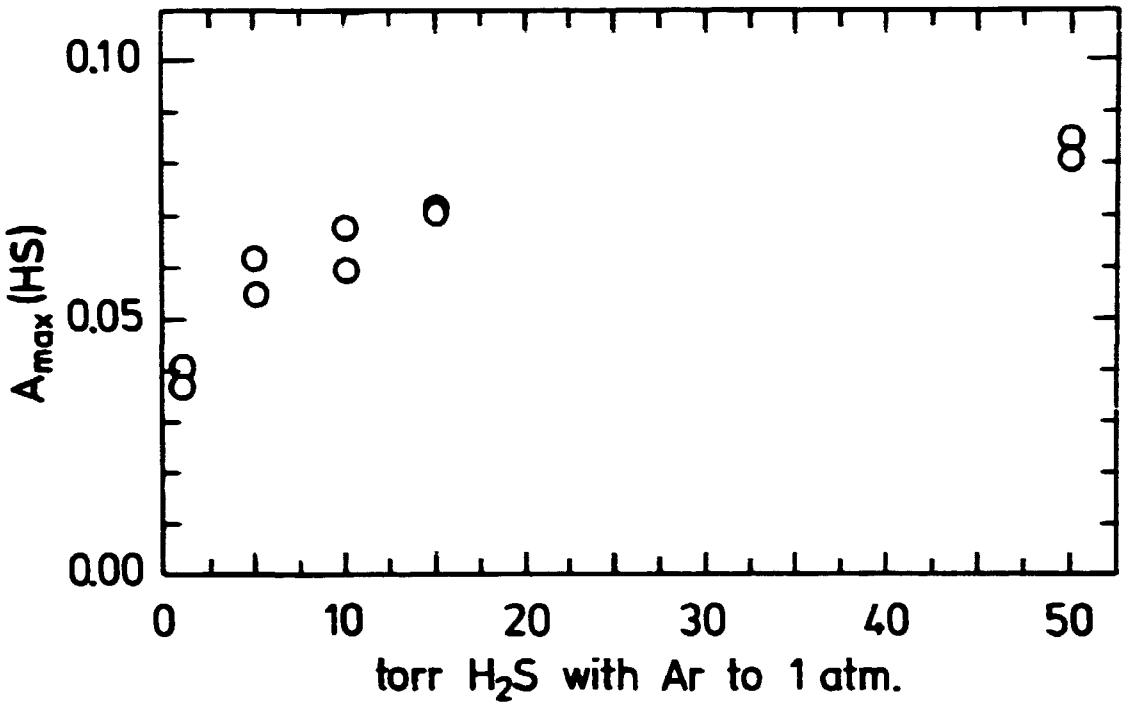

Fig. 8. Yield of HS in H_2S/Ar mixtures measured by the maximum HS absorbance at 3241 Å.

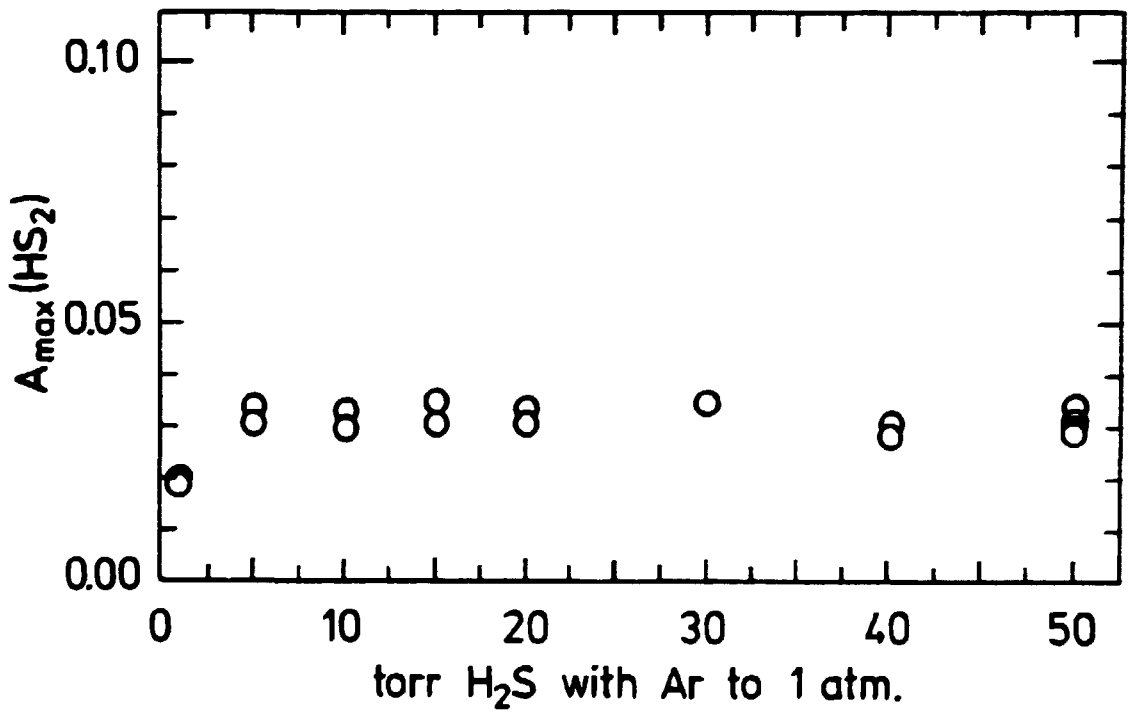

Fig. 9. Yield of HS_2 in H_2S/Ar mixtures measured by the maximum HS_2 absorbance at 3448 Å.

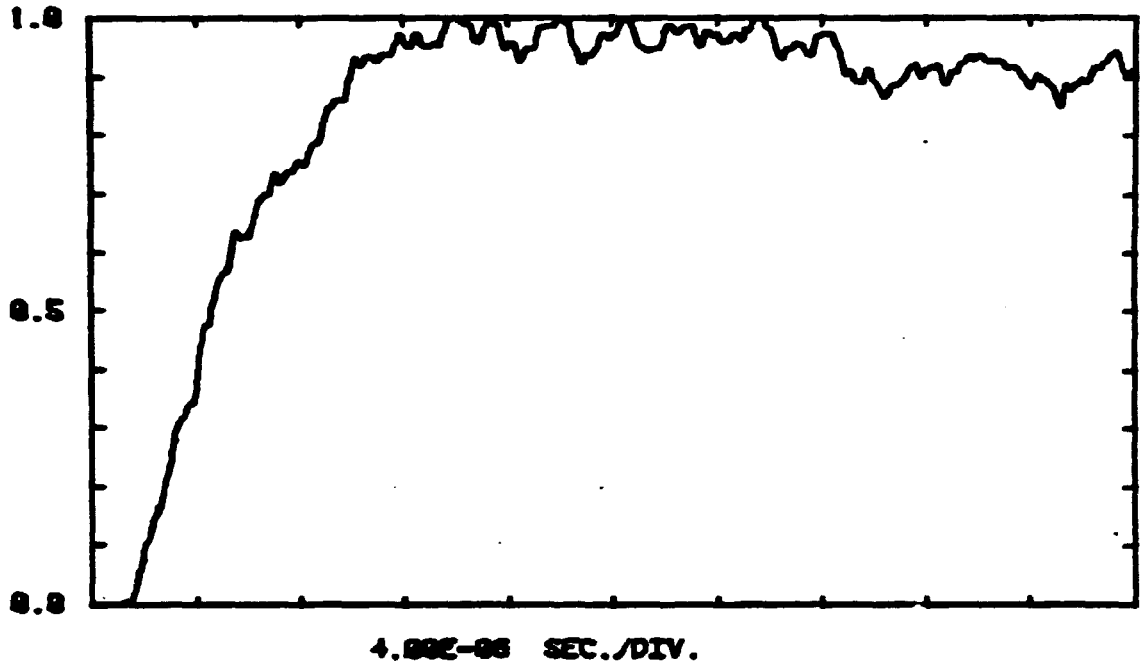

Fig. 10. Experimental HS formation in 5 torr H_2S with H_2 to 760 torr. Monitored at 3241 Å. T = 295 ± 1 K.

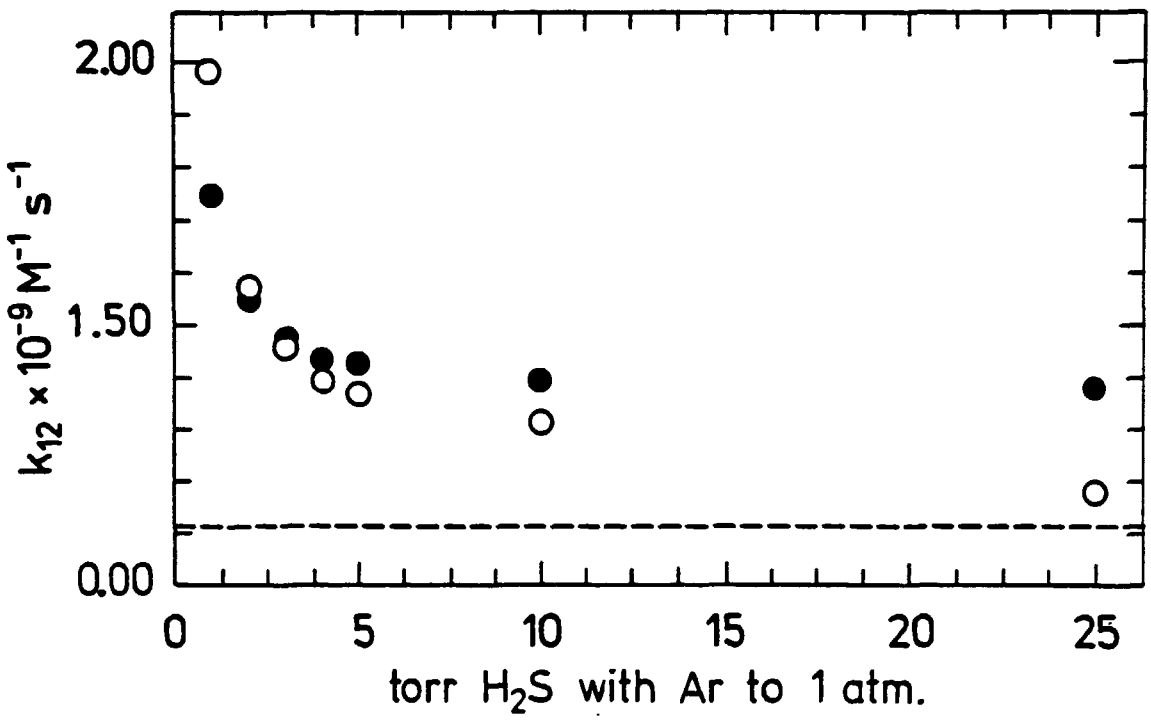

Fig. 11. Comparison between experimentally determined values (o) of $k(H + H_2S \rightarrow H_2 + HS)$ determined from $k = \ln 2/(\tau_f \cdot c_o)$ in H_2S/H_2 mixtures (τ_f if the formation half-life of HS and c_o the initial H_2S concentration) with values (o) derived from a theoretical model including H and HS consuming reactions : $H + H \overset{M}{\rightarrow} H_2$, $H + HS \rightarrow H_2 + S$, and $HS + HS \rightarrow$ products. The assymptote indicates the first order value.

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Title and author(s)

CHEMICAL KINETICS IN THE GAS PHASE
PULSE RADIOLYSIS OF HYDROGEN SULFIDE SYSTEMS

Ole John Nielsen

Date December 1979

Department or group

Chemistry Dept.

Group's own registration number(s)

35 pages + tables + illustrations

Abstract

Formations and decays of HS and HS_2 radicals in the gas phase pulse radiolysis of pure H_2S, H_2S/Ar and H_2S/H_2 systems have been followed directly by kinetic spectroscopy. The literature on the subject is reviewed and a complete reaction scheme is discussed. Computer-simulations have been used to check the validity of the proposed mechanisms. Rate constants $k_{HS+HS}=(2.0 \pm 0.4) \times 10^{10}\ M^{-1}s^{-1}$ and $k_{H+H_2S}= (6.0 \pm 1.2) \times 10^{8}\ M^{-1}s^{-1}$ have been determined. The reaction of HS radicals with S atoms is responsible for the HS_2 formation. Pseudo-first order rate constants for reactions of HS with 1.3 butadiene, ethylene and molecular oxygen are reported.

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