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# PHOTOLYSIS OF HYDROGEN SULPHIDE IN LOW-TEMPERATURE MATRICES

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## ABSTRACT

Photolysis of hydrogen sulphide in argon, nitrogen and carbon monoxide matrices at 20 K produces HS radicals and S atoms. On warming the matrix, $H_2S_2$ and $S_2$ molecules are formed as a result of recombination reactions. The latter are identified by a blue-purple emission observed during warm-up of the matrix.

## INTRODUCTION

The photolysis of hydrogen sulphide has been used as a source of hydrogen atoms in low-temperature matrices [1]. In a carbon monoxide matrix, photolysis of hydrogen sulphide gave the formyl radical HCO but no evidence was found for the production of HS radicals. In an argon matrix, on the other hand, Milligan and Jacox [1] identified ultra-violet absorptions due to HS after the photolysis of hydrogen sulphide. More recently, Acquista and Schoen [2] examined the photolysis of hydrogen sulphide in an argon matrix and reported an infrared absorption at 2541 $cm^{-1}$, as well as ultra-violet absorption at ca. 329 nm, due to the HS radical. As part of a series of photochemical studies in low-temperature solids, we have re-examined the photolysis of hydrogen sulphide in argon and carbon monoxide matrices, and extended the work to nitrogen matrices.

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## EXPERIMENTAL

The cryogenic apparatus and procedure have been described previously [3]. The photolysis experiments were carried out with a Philips medium pressure mercury lamp, either during deposition of the matrix or in situ after deposition. Infrared spectra of the matrices were recorded, using a Perkin–Elmer 225 spectrometer, before and after photolysis and after carrying out diffusion experiments by warming the matrix to 30-40 K for a few minutes and then recooling to 20 K.

## RESULTS

A weak absorption at 2541 cm$^{-1}$ was observed after photolysis of hydrogen sulphide in an argon matrix at M/A = 1000, corresponding to the value reported by Acquista and Schoen [2] for the HS radical. No absorption could be detected after photolysis of more concentrated argon matrices because of overlap by the hydrogen sulphide stretching mode absorptions of multimers. In nitrogen and carbon monoxide matrices the hydrogen sulphide multimer spectrum is less extensive at M/A = 1000, since these matrices are more "rigid" at 20 K, thus photolysis experiments gave more satisfactory results. In a nitrogen matrix a pair of bands due to the HS radical was observed at 2551 and 2553 cm$^{-1}$, the latter being weaker and presumably resulting from an alternative trapping site, while in carbon monoxide a band was found at 2544 cm$^{-1}$ (Fig. 1). Intense absorptions due

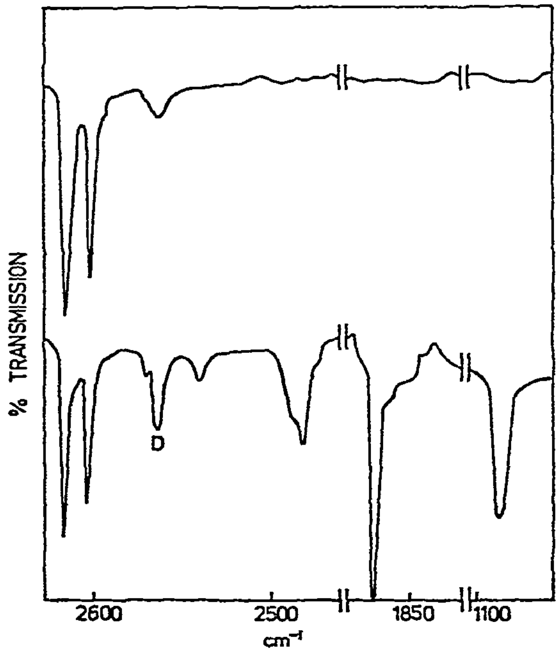

Fig. 1. Infrared spectra before and after photolysis of hydrogen sulphide in a carbon monoxide matrix at M/A = 1000. The band labelled D is due to hydrogen sulphide dimer.

to the HCO radical, at 2489, 1861 and 1091 $cm^{-1}$, were also observed after the photolysis of hydrogen sulphide in carbon monoxide matrices.

On warming a photolysed matrix to about 30 K, a blue purple glow appeared which lasted for several minutes. This emission was completely independent of the matrix material used, i.e. argon, nitrogen or carbon monoxide, and of the concentration of hydrogen sulphide in the matrix. The emission was observed after in situ photolysis as well as after photolysis during deposition. Control experiments in which the matrix materials were deposited alone, and with various possible impurities (such as carbon dioxide) added, did not result in any emission after irradiation and warm-up. Addition of carbon dioxide to a matrix of hydrogen sulphide in argon caused no change in the observed emission. Thus the emission must result from the photolysis products of hydrogen sulphide. If the matrix is cooled to 20 K after the emission has started, the glow ceases but recommences on warming to 30 K. Infrared spectra of the matrix recooled to 20 K after the emission had ceased showed no significant reduction in the intensities of the bands due to the HS radical.

Further diffusion at higher temperatures (ca. 40 K) resulted in the appearance of a number of new absorptions and the concurrent disappearance of the bands due to the HS radical. Many of the new bands in the 2600–2500 $cm^{-1}$ region may be assigned to hydrogen sulphide multimers [3], but an absorption at 2513 $cm^{-1}$ is to lower frequency than any hydrogen sulphide multimer absorption and must therefore be assigned to a different hydrogen-sulphur species. Weak bands at 912 and 864 $cm^{-1}$ are also produced on diffusion.

## DISCUSSION

Absorption of ultra-violet radiation by hydrogen sulphide in the broad absorption continuum from 270 to 190 nm can result in two alternative primary photolytic processes

$$H_2S + h\nu \rightarrow H + HS \tag{1}$$

$$H_2S + h\nu \rightarrow H_2 + S \tag{2}$$

the first of these being favoured [4]. The comparatively low yield of HS radicals may be accounted for by photo-dissociation of the HS radical through absorption at ca. 329 nm

$$HS + h\nu \rightarrow H + S \tag{3}$$

Hydrogen atoms are relatively mobile at 20 K [5], thus being removed by reactions such as

$$H + H_2S \rightarrow H_2 + HS \tag{4}$$

$$H + HS \rightarrow H_2 + S \tag{5}$$

Sulphur atoms, on the other hand, are much larger and correspondingly less mobile; they will thus remain trapped in the matrix at 20 K. Warming the matrix to temperatures around 30 K does not cause sufficient softening to allow extensive diffusion of HS radicals (the intensities of the bands due to HS are not significantly reduced), but plausibly permits migration of sulphur atoms, which are present at relatively high concentration, resulting in the formation of $S_2$ molecules

$$S+S \rightarrow S_2 \tag{6}$$

Brewer and Brabson [6] have observed fluorescence in the violet region of the spectrum from $S_2$ molecules in low-temperature matrices on irradiation with a mercury arc. Thus it seems reasonable that the recombination process (6) results in the fluorescent emission observed in the present work. Confirmatory evidence of the production of sulphur is provided by the fact that the low-temperature matrix support window was covered with a film of poor thermally conducting material after a photolysis experiment, which had to be cleaned off before a further matrix isolation experiment could be performed.

Warming the matrix to higher temperatures (ca. 40 K) permits diffusion of the HS radicals, resulting in the formation of hydrogen persulphide and possibly higher analogues

$$HS+HS \rightarrow H_2S_2 \; (+HS \rightarrow H_3S_3 \text{ etc.}) \tag{7}$$

The bands observed to appear after diffusion of photolysed hydrogen sulphide matrices at 40 K are compared with the gas and solid phase infrared frequencies of hydrogen persulphide in Table 1. It can be seen that, when allowance is made for matrix shifts [7], all the bands may be assigned to the three most intense absorptions of hydrogen persulphide.

TABLE 1

COMPARISON OF BANDS OBSERVED AFTER DIFFUSION OF PHOTOLYSED HYDROGEN SULPHIDE MATRICES WITH THE INFRARED SPECTRUM OF HYDROGEN PERSULPHIDE

| *$H_2S_2$* | | *Observed* |
|---|---|---|
| *mode* | *$\nu$ ($cm^{-1}$)*[a] | *$\nu$ ($cm^{-1}$)* |
| $\nu_5$ | 2558.6 s | 2513 |
| $\nu_1$ | 2555.8 w | |
| $\nu_6$ | 886 vs | 912 |
| $\nu_2$ | 868 s | 864 |
| $\nu_3$ | 501 w | |
| $\nu_4$ | 416 w | |

[a] B. P. Winnewisser, *J. Mol. Spectrosc.*, 36 (1970) 414;
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N. Zengin and P. A. Giguere, *Can. J. Chem.*, 37 (1959) 632.

Thus the primary photolytic products of hydrogen sulphide in matrices are HS radicals, sulphur atoms and, by inference, hydrogen. Reactions on warm-up lead to the formation of $S_2$ molecules and hydrogen persulphide.

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