THE STABILITY OF EMITTED ODOUROUS COMPOUNDS IN THE ATMOSPHERE

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Abstract -   This report contains a survey of reactions which are of
consequence for the stability of malodourous compounds in the air. The
compounds dealt with are hydrogen sulphide, methyl mercaptan, ethyl
mercaptan, dimethyl sulphide and dimethyl disulphide. Estimated time of
atmospheric residence of hydrogen sulphide and dimethyl sulphide are
reported, together with the present knowledge as to their removal from
the atmosphere.

INTRODUCTION

When studying odour emissions and dispersion in the atmosphere, it is
essential to know if and to what extent the odourous compounds are con-
verted in the air. Conversions of physical or chemical nature may not
only reduce the odour, but may in some cases even enhance it (Lindvall
ed. 1970). The stability of the odourous compounds in the atmosphere,
however, has been studied only to a very limited extent. The most
important group of odourous compounds from industrial as well as from
natural sources are the volatile reduced sulphur compounds such as
hydrogen sulphide, methyl mercaptan, ethyl mercaptan, dimethyl sulphide
and dimethyl disulphide. The main sources of these compounds are kraft
pulp mills, fish meal plants, refineries and manure handling.

This study will be concerned only with the stability of the reduced
sulphur compounds. Few investigations have been made of their atmospheric
behaviour; it has therefore been necessary to include reactions that
are or might be of importance for the atmospheric chemistry of these
compounds.

REACTIONS OF IMPORTANCE FOR THE AIR CHEMISTRY OF HYDROGEN SULPHIDE
AND ORGANIC SULPHUR COMPOUNDS

1. Reactions with ozone

The reaction of hydrogen sulphide with ozone in air has been in-
vestigated by Cadle and Ledford (1966) and by Hales et al. (1969):

$$H_2S + O_3 \longrightarrow H_2O + SO_2$$

Cadle and Ledford studied this reaction in a flow system and found
the reaction orders to be near zero for hydrogen sulphide and 1.5
for ozone. The rate law followed was:

$$k = 2.5 \cdot 10^8 \exp(-8300/RT) \; cm^{1.5} \; mole^{-0.5} \; sec^{-1}$$

By changing the surface-to-volume ratio it was found that the
reaction was at least partially heterogenous.

Hales et al. measured the reaction rate in two tubular, laminar
flow reactors. They obtained the same reaction order for ozone as
Cadle and Ledford, but 0.5 for hydrogen sulphide. The rate of
generation of sulphur dioxide was found to be

$$\frac{d \, C_{SO_2}}{dt} = 22.8 \exp(-6500/RT) \; C_{H_2S}^{0.5} \cdot C_{O_3}^{1.5} \; \mu mole/litre \cdot min.$$

Comparison of data from the two tubular reactors indicated that
the reaction was almost totally homogenous.

Kirchner et al. (1971) studied the reaction of ethyl mercaptan with
ozone in ppm concentrations in a flow reactor. The rate constant
was determined by examining competitive reactions. Hexene and iso-
butene were used as comparison reactants, and the reaction products
were determined by gaschromatographic analysis. Rate constants,which
were taken from literature, of the hexene and isobutene reactions
with ozone were used, and the reaction rate of ethyl mercaptan and
ozone was determined:

$$k = (2.4 \pm 0.8) \cdot 10^3 \; litre/mol \qquad (30^\circ C)$$

2. Reactions with atomic oxygen (O)

The reaction of hydrogen sulphide with atomic oxygen has been studied by Sharma et al. (1965, 1967) and by Liuti et al. (1966). The tests were performed in an argon - oxygen atmosphere, in which the atomic oxygen is produced by a microwave discharge or by a dc-discharge tube, but the results should be applicable also to air.

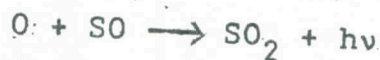The reaction was considered to follow the mechanism

$$\text{initial reaction: } O + H_2S \longrightarrow OH + SH$$

followed by the chain reactions:

$$O + OH \longrightarrow O_2 + H$$
$$H + H_2S \longrightarrow H_2 + SH$$

or totally:

$$H_2S + O \longrightarrow H_2 + SO$$

It continues:

$$O + SO \longrightarrow SO_2 + h\nu$$
$$O_2 + SO \longrightarrow SO_2 + O$$

The initial reaction rate was determined by Liuti et al. (op.cit.) to be

$$k = (4 \pm 2) \cdot 10^{-14} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad \text{(at room temperature)}$$

According to Hollinden et al. (1970), using a helium-oxygen atmosphere, the initial reaction rate was

$$k = (1.74 \pm 0.40) \cdot 10^{11} \exp(-[1500 \pm 100]/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

3. Oxidation with oxygen (O_2)

Boström (1967) examined the reactions of hydrogen sulphide and found that no oxidation occurs below 500°C without a catalyst. In the water phase, however, H_2S is readily oxidized, and the oxidation products vary with the pH of the solution. Alferova et al. (1967) observed that at pH below 10, H_2S was partially evolved with the spent air. Within the pH range of 7 - 13.75, the main oxidation

product was thiosulphate. At a pH value of 8, sulphite was one of the products. The concentration of sulphate increased with increasing pH, and at pH values below 12.6 sulpate was the main oxidation product. Many of the substances present in airborne matter act as oxidizing catalysts.

The gas phase reaction of methyl mercaptan with oxygen was studied by Harkness and Murray (1966) at temperatures over $200^\circ C$; below that temperature, the reaction proved to be very slow and thus negligible.

As observed for H_2S, liquid phase oxidation of methyl mercaptan can occur at room temperature. The oxidation products vary with the pH of the solution. At pH values below 11, methyl mercaptan was partially converted to methanol (Alferova et al.,op.cit.).

4. Photolysis

Hydrogen sulphide has a strong absorption band between 2700 and 1800 Å. Photolysis in this region was studied by Gann and Dubrin (1967); the initial reaction was found to be

$$H_2S + h\nu \ (2138 \ \text{Å}) \longrightarrow H + SH$$

Nearly all the initial electronic energy of the system is converted to the kinetic separation of the H and SH. However, the continuation of the reaction has not been investigated.

Steer et al. (1967) and Steer and Knight (1968) studied the photolysis of pure methyl mercaptan at wavelengths > 2300 Å. The photolysis seemed to follow the mechanism

$$CH_3SH + h\nu \longrightarrow CH_3S + H$$

$$H + CH_3SH \longrightarrow H_2 + CH_2S$$

$$2 \ CH_3S \longrightarrow CH_3 \ SS \ CH_3$$

In addition to hydrogen and dimethyl disulphide, also methane, hydrogen sulphide and dimethyl sulphide were observed as reaction products. Photolysis of methyl mercaptan in the atmosphere is likely to produce several other products as well.

Rayner and Murray's (1970) experiments show that the photolytic oxidation of methyl mercaptan exposed to sunlight is fairly slow. After exposure for 9 days to radiation of 3600 Å and 2537 Å, 35 % and 32% respectively remained of the initial concentration of approx. 1000 ppm.

The primary processes in flash photolysis of methyl mercaptan at approx. 1950 Å were investigated by Callear and Dickson (1970). Two primary processes were identified:

$$CH_3SH^* \nearrow CH_3S + H \\ \searrow CH_3 + SH$$
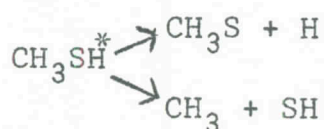
Flash photolysis of ethyl mercaptan at the same wavelength was considered to follow

$$C_2H_5SH^* \nearrow C_2H_5 + SH \\ \searrow C_2H_5S^* + H$$
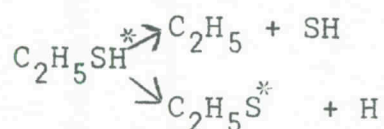
Rayner and Murray (op.cit.) also studied the photolytic oxidation of dimethyl sulphide and dimethyl disulphide. Exposure of DMS to long wavelength radiation (3600 Å) showed that 96.5 % of the initial concentration (approx. 1000 ppm) remained after 9 days, whereas after exposure for 15-18 hours to short wavelength radiation (2537 Å) the destruction was total.
After DMDS was exposed to long wavelength radiation for 9 days, 2% of the initial concentration was left, whereas short wavelength radiation converted all the DMDS in 48-52 minutes.

Bentley et al. (1972) observed that photolysis of DMS for 6.63 hours at a temperature of $24 \pm 2^\circ C$ at wavelengths >654 Å in the air resulted in a $91 \pm 4\%$ conversion of the initial concentration (68 mg/l) The products identified were CH_3SOCH_3, $CH_3SO_2CH_3$, CH_3SO_3H, CH_3SSCH_3,
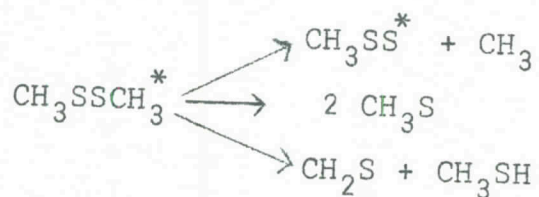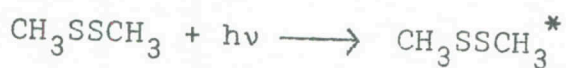
$CH_3SO_2SCH_3$, SO_2, SO_3, CH_3OH, HCHO, HCOOH and $HCOOCH_3$.

Photolysis of a similar mixture of DMS in the air at wavelengths >2600 Å required 12 hours' exposure to convert 91 $\pm$4% of the concentration. The same products were identified but the product distribution was somewhat different.

Both direct photo oxidation of DMS and photochemical cleavage of the carbon-sulphur bonds seemed to be involved. The differences in the product distribution were considered to be due to generation of oxygen atoms and ozone by high energy UV-light.

Callear and Dickson (op.cit) studied the primary processes in flash photolysis of DMS and DMDS at ~1950 Å. The primary processes were considered to be

$$CH_3SCH_3 + h\nu \longrightarrow CH_3 + CH_3S$$

and

$$CH_3SSCH_3 + h\nu \longrightarrow CH_3SSCH_3^*$$

$$CH_3SSCH_3^* \begin{cases} \longrightarrow CH_3SS^* + CH_3 \\ \longrightarrow 2\ CH_3S \\ \longrightarrow CH_2S + CH_3SH \end{cases}$$

5. Thermal decomposition

Boström (op.cit), when studying the reactions of H_2S, found this gas to be stable at 25°C. Thermal decay could not be observed at temperatures lower than 350°C. In the presence of catalysts, however, the reaction $H_2S \longrightarrow H_2+S$ occurred already at room temperature.

6. Reactions with sulphur dioxide

The reactions of hydrogen sulphide with sulphur dioxide have been investigated by Surnina (1961), Barbieri and Ricerca (1960) and by Croatto and Barbieri (1964).

There are two major reactions:

1) $2H_2S + SO_2 \longrightarrow \frac{3}{8} S_8 + 2H_2O$

2) $H_2S + SO_2 + H_2O \longrightarrow H_2S_xO_6$

where x varies between 3 and 12
(Wackenroder reaction)

Reaction 1) can occur in the gas as well as in the liquid phase, water vapour being required for the gas phase (Surnina, op.cit), whereas reaction 2) occurs in water solution.
Croatti and Barbieri (op.cit) report a mechanism for reaction 1) in water solution. The reaction takes place in solutions with a pH value >3.
Barbieri and Bruno (op.cit) made chromatographic investigations of the mechanism of reaction 2), using H_2S labelled with S^{35}.
They found that HS_xOH was a probable intermediate in the reaction.

CONCLUSIONS OF OBSERVATIONS AT ATMOSPHERIC CONDITIONS

Junge (1963), using the results of Cadle and Ledford (op.cit), calculated the lifetime of H_2S in atmospheric ozone concentrations of 50 µg/m to be approx. 1.7 days.
In the study carried out by Robinson and Robbins (1970), the lifetime of H_2S in urban atmosphere was about 2 hours, whereas in unpolluted air it was about 2 days.

Krasovitskay et al. (1965) investigated the decrease of certain air pollutants with increasing distance to a group of oil processing and petrochemical plants. The results showed that the decrease in H_2S concentration was more rapid than that of the other compounds studied (SO_2, CO and hydrocarbons).

Verzár and Evans (1959) found that a large number of Aitken nuclei were formed in outdoor sun-irradiated air and that this particle formation was enhanced by the presence of hydrogen sulphide. This indicated that a direct oxidation of hydrogen sulphide occured.

Cadle and Allen (1971) point out that hydrogen sulphide is likely to be oxidized in water droplets in the air. This may be a very fast reaction; however it has not been the subject of any specific studies.

Lovelock et al. (1972) discussed the atmospheric residence time of dimethyl sulphide and found one week to be a probable duration of residence.

REMOVAL OF H_2S AND ORGANIC SULPHUR COMPOUNDS FROM THE GAS PHASE BY ADSORPTION

Adsorption of H_2S and organic sulphur compounds on airborne particles, fog droplets and on the ground no doubt plays an important role in the removal of these compounds from the atmosphere, but it has not, so far, been paid much attention.

As already mentioned, hydrogen sulphide can be dissolved in atmospheric water droplets and presumably be oxidized in solution.

The photochemical oxidation of dimethyl sulphide leads mainly to dimethyl sulphoxides, methane sulphonic acid, sulphur dioxide and sulphuric acid. Dimethyl sulphoxide is volatile and of a hygroscopic nature and is therefore likely to be scavenged from the air by rain or lost through surface adsorption. Methane sulphonic acid has physical properties resembling those of sulpuric acid and can thus be assumed to have the same atmospheric lifetime as sulphuric acid aerosol (Lovelock et al.,1972).

DISCUSSION

From this survey it is obvious that very little is known about the atmospheric chemistry of the odourous compounds. The main reason is probably that it is uncertain today which parameters, in addition to the concentration of the compounds, must be determined in order to obtain the complete picture of the kinetics. Up to now there has been no method available sensitive enough to measure the low concentration ranges of interest in ambient air. However, the recently developed instrumental techniques for analysis of gaseous sulphur compounds have made it possible to detect concentrations close to the odour threshold. The flame photometric detector (FPD) (Brody and Chaney, 1966) is probably the most suitable instrument for studies of odour pollution. Like the human nose, it operates with momentaneous sampling. The flame photometric technique has been used for ambient air measurements of sulphurous compounds (Lövblad and Grennfelt, 1973), but it has not been possible to use the results in studies on stability.

It is evident that measurements of the concentrations of odourous substances will provide only part of the explanation of their atmospheric behaviour. Many factors such as the presence of other pollutants, air temperature, and relative humidity will contribute to the conversion of these compounds in the air. A satisfactory investigation of their stability in the atmosphere will probably require studies in the laboratory followed by affirmative field studies

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