THE GASEOUS OXIDATION OF ALKANE THIOLS

BY C. F. CULLIS AND L. C. ROSELAAR * Chemistry Dept., Imperial College, London, S.W.7

Received 6th June, 1958

The gaseous oxidation of ethane and methane thiols has been studied in the temperature range 210-260°C. In the slow combustion of both compounds, oxygen has a positive influence on the oxidation rate while the thiol has a well-defined retarding effect. Sulphur dioxide is always produced in copious quantities and other products include aldehydes, methanol and carbon monoxide; dialkyl disulphides are believed to be formed in oxygen-lean systems.

It is suggested that initial oxygen attack occurs at the SH group resulting in the formation of an RS radical. These radicals are then believed either to combine with one another in a chain-terminating reaction or to react with oxygen to form sulphur dioxide and alkyl radicals, which subsequently undergo further oxidation.

Organic sulphur compounds are present in most sources of natural petroleum ¹ and are known to be responsible for promoting "knock"² as well as reducing the anti-knock effect of lead tetraethyl.³ Among the most powerful sulphurcontaining "knock" promoters are the alkane thiols, whose presence is also undesirable on account of their intense and disagreeable smell and their corrosive action. In addition their oxidation products include sulphur dioxide which is harmful to animal and vegetable life. For these reasons a variety of methods have been developed for the removal of thiols from petroleum.⁴

The pro-knock action of organic sulphur compounds is presumably linked up with the mechanism of their gaseous oxidation and it was to elucidate this mechanism that a study was made of the slow combustion of ethane thiol and methane thiol. Previous investigations of the gaseous reactions of thiols have been confined to their photolysis 5, 6 and pyrolysis.7, 8, 9

EXPERIMENTAL

MATERIALS

Commercial samples of the thiols (obtained from B.D.H. Ltd.) were carefully fractionated before use and after introduction into the apparatus were freed from dissolved gases by repeated melting and freezing under vacuum. Oxygen was obtained from a cylinder and was purified by passage through traps surrounded by liquid oxygen which removed carbon dioxide and water vapour.

APPARATUS

A conventional static apparatus was used, the reactants being admitted to a cylindrical pyrex reaction vessel (10 cm long and 6 cm diam.). This was initially rinsed with concentrated nitric acid followed by water and was then heated under vacuum at 450°C for several hours. The course of the reaction was followed manometrically, the contents of the reaction vessel being withdrawn by connecting it with two evacuated traps surrounded by liquid nitrogen. All gases and vapours were drawn through the traps by a Töpler pump, the vapours being condensed and the permanent gases being transferred to a gas pipette for subsequent analysis.

A standardized evacuation procedure was adopted and it was found that reproducibility of results was achieved with both thiols after the reaction vessel had become acclimatized (*ca.* 20 runs).

* present address : Department of Chemistry, South-East Essex Technical College.

ANALYTICAL PROCEDURE

After a run, the traps contained ca. 0.01 mole material. For the analysis of all condensables except sulphur dioxide and residual thiol, the contents were dissolved in 25 ml water. For estimation of the two sulphur compounds the solvent was 0.005 N sodium hydroxide in 40 % ethanol. The function of the sodium hydroxide was to assist solution of the thiol. The ethanol too was helpful in this respect and also retarded oxidation of sulphur dioxide.

Pressure measurements were found to yield little information regarding the progress of reaction and therefore in the early stages of the investigation of each system, spot tests ¹⁰ were used to detect and to determine approximately the most important reaction products. For more accurate analysis it was necessary to use methods which were sensitive enough to estimate the small amounts of each compound present and which were not affected by the other constituents of the mixture. A summary of the methods finally adopted is given in table 1.

TABLE 1

compound method of estimation titration with silver nitrate in ammoniacal solution, with sodium nitro-RSH prusside as indicator 11 $(RSH + AgNO_3 = RSAg + HNO_3)$ measurement of colour developed on reaction with formaldehyde and SO₂ basic fuchsin in dilute sulphuric acid, thiol being removed previously by addition of mercuric chloride 12 $(RSH + HgCl_2 = RSHgCl + HCl)$ total treatment with excess sodium bisulphite and titration with iodine of the aldehydes combined bisulphite liberated from the complex 13 $(RCHO + NaHSO_3 \rightleftharpoons RCH(OH)SO_3Na)$ **HCHO** measurement of colour developed on reaction with modified Schiff's reagent 14 total organic direct titration with alkali, allowance being made for sulphur dioxide acids present CH₃OH destruction of readily oxidizable material by distillation with hydrogen peroxide, oxidation of methanol to formaldehyde and measurement

of colour developed on reaction with chromotropic acid ¹⁵

O₂, CO, CH₄ conventional gas analysis

RESULTS

ETHANE THIOL

Ethane thiol is oxidized slowly at 218° C, reaction being accompanied by a small decrease in pressure. Analytical results (fig. 1 and 2) indicate that over the first 20-25 % of reaction the rate of consumption of thiol increases exponentially with time. Table 2(a) shows how the initial and maximum rates of disappearance of ethane thiol vary with the

TABLE 2.—DEPENDENCE OF RATE OF OXIDATION ON INITIAL REACTANT PRESSURES

RSH (mm)	O2 (mm)	initial rate (mm min ⁻¹)	maximum rate (mm min ⁻¹)
	(a) eth	ANE THIOL	
200	160	0.4	1.4
200	320	1.4	3.6
200	240	0.8	2.4
100	240	0.5	3.2
	(<i>b</i>) met	HANE THIOL	
200	160	0.2	0.9
200	320	2.0	3.3
100	320	2.6	8.0

pressures of the reactants in four typical systems. The reaction is markedly accelerated by increasing oxygen pressure, while the thiol appears to have an inhibiting effect on its own oxidation.

Fig. 1 shows the course of the reaction in the presence of a deficit of oxygen. The ethane thiol and oxygen are consumed in closely parallel fashion, 140 mm thiol reacting with 150 mm oxygen to produce 60 mm sulphur dioxide, 40 mm aldehyde and 20 mm acid. Only trace amounts (< 1 mm) of formaldehyde, methanol and carbon monoxide are detectable and hydrogen sulphide is absent. The aldehyde is presumably acetaldehyde and the acid is peracetic acid or acetic acid produced by further oxidation of the



FIG. 1.--The oxidation of ethane thiol.

Temp. 218°C; ethane thiol pressure 200 mm; oxygen pressure 160 mm. ○ ethane thiol; ● oxygen; ④ sulphur dioxide; ④ total aldehydes; ● total acids;

aldehyde. If it is assumed that peracetic acid is unstable at this temperature, 16 the following equations represent the overall reaction:

$$40(C_2H_5SH + 2O_2 = CH_3CHO + H_2O + SO_2),$$

$$20(C_2H_5SH + 2AO_2 = CH_3COOH + H_2O + SO_2).$$

80 mm thiol and 20 mm oxygen thus remain unaccounted for, and the ratio 4:1 suggests that in addition to the occurrence of the above two reactions, diethyl disulphide is formed according to the equation:

$$20(4C_2H_5SH + O_2 = 2C_2H_5S \cdot S \cdot C_2H_5 + 2H_2O).$$

These three equations involve a pressure decrease of 30 mm which may be compared with the experimental value of 25 mm (fig. 1). Attempts were made to detect disulphide by reduction to thiol ¹⁷ but no conclusive results were obtained.

Fig. 2 illustrates the course of reaction for a mixture containing more oxygen. In this system, acetaldehyde is clearly formed as an intermediate, for considerable quantities of its further oxidation products also accumulate, viz., 20 mm carbon monoxide, 5 mm formaldehyde and 15 mm methanol. Here the sulphur is completely converted into sulphur dioxide and there is a perfect sulphur balance throughout. There is, however, a considerable carbon deficit. In order to detect carbon dioxide, ethane and ethylene, the final products were drawn through traps surrounded by solid carbon dioxide instead of by liquid nitrogen. Nevertheless the only additional product found in this way was ethylene (*ca.* 5 mm), and the larger part of the carbon thus remains unaccounted for.





Temp. 218°C; ethane thiol pressure 100 mm; oxygen pressure 240 mm. ○ ethane thiol; ● oxygen; ● sulphur dioxide; ● total aldehydes; □ formaldehyde; △ methanol; ▲ carbon monoxide; ---- pressure change.

METHANE THIOL

Methane thiol is oxidized with more difficulty than ethane thiol but reaction proceeds at a convenient rate at 257° C. Table 2(b) shows that the dependence of oxidation rate on the reactant pressures is essentially the same as with the higher homologue.

In an oxygen-lean system (fig. 3), the two reactants are again consumed in parallel fashion, 140 mm thiol reacting with 130 mm oxygen to give 90 mm sulphur dioxide together with smaller amounts (5-15 mm) of carbon monoxide, formaldehyde, methanol and methane. In this system, also, no hydrogen sulphide is detected. Here too then there is an appreciable sulphur deficit which, in view of the small amount of oxygen available, is probably due to disulphide formation. In addition, there is throughout a considerable carbon deficit.

Fig. 4 shows that the behaviour of an oxygen-rich mixture of methane thiol is similar to that observed with the ethane derivative. At the end of reaction, complete conversion to sulphur dioxide has taken place, although at intermediate stages, some of the combined sulphur cannot be accounted for. The total yield of carbon compounds found, viz., 40 mm carbon monoxide, 10 mm formaldehyde, 25 mm methanol and traces of methane leaves a carbon deficit of 25 mm.

DISCUSSION

INITIAL ATTACK

While it is difficult to make quantitative comparisons of the reactivities of compounds whose behaviour has been studied under widely differing conditions, the two lowest thiols are evidently much more readily oxidized than the parent



FIG. 3.—The oxidation of methane thiol.



alkanes. In other words, the introduction of the "foreign" group appears to enhance the reactivity of the hydrocarbon molecule towards oxygen. In this respect, thiols are similar to other alkane derivatives, such as chloralkanes,¹⁴ ethers,¹⁹ ketones,²⁰ esters,²¹ amines,²² aldehydes,²³ and the lower alcohols.²⁸ When the substituent group contains hydrogen, this group may itself form the point of attack in the resulting compound; this occurs, for example, when the substituent is CHO. In other cases, the substituent group is comparatively inert and oxidation continues to take place at a point on the hydrocarbon chain.²⁵

The formation of copious quantities of sulphur dioxide from the beginning of reaction strongly suggests that with the thiols the SH group itself suffers initial attack and does not merely activate the adjacent alkyl group. The similar kinetic behaviour observed for ethane thiol and methane thiol (table 2) indicates that the two compounds are oxidized by analogous mechanisms, both of which involve initial hydrogen abstraction from the SH group:

$$RSH + O_2 \rightarrow RS + HO_2. \tag{1}$$

277

The HO₂ radical probably attacks another molecule to form hydrogen peroxide :

$$RSH + HO_2 \rightarrow RS + H_2O_2, \tag{2}$$

which, in solution, will tend to oxidize both sulphur dioxide and unchanged thiol. The perfect sulphur balances obtained at the end of the reaction in both oxygenrich systems studied (fig. 2 and 4) suggest that very little hydrogen peroxide is



Temp. 257°C; methane thiol pressure 100 mm; oxygen pressure 320 mm. ○ methane thiol; ● oxygen; ④ sulphur dioxide; □ formaldehyde; △ methanol; ▲ carbon monoxide; ---- pressure change.

in fact formed. It seems probable therefore that once oxidation has been initiated by reaction (1), other radicals produced in later stages of the reaction are responsible for primary attack, e.g.,

$$RSH + CH_3O \rightarrow RS + CH_3OH.$$
(3)

Independent evidence that SH groups are readily attacked by oxygen is provided by the fact that hydrogen sulphide is oxidized at quite low temperatures.²⁶

THE RS RADICAL

Reactions (1) and (3) produce an RS radical, the existence of which in the gas phase 27, 28 and in solution 29 has previously been postulated by other workers. By analogy with alkoxy radicals 30, 31 these might be expected to decompose to yield thioaldehydes :

$$RCH_2S^{\bullet} \rightarrow RCHS + H,$$
 (4)

$$RCH_2S^{\bullet} \rightarrow CH_2S + R.$$
 (5)

OXIDATION OF ALKANE THIOLS

In view, however, of the marked thermal instability of the latter compounds, they are unlikely to be formed as final oxidation products.

The reluctance of the CH₃S and C₂H₅S radicals to decompose is paralleled by the comparative stabilities of the methoxy and ethoxy radicals ³¹ and is also supported by the results of other workers.^{27, 28} The main reaction of RS radicals in the systems studied is thus believed to be association with oxygen to yield directly sulphur dioxide and an alkyl radical:

$$RS + O_2 \rightarrow R + SO_2. \tag{6}$$

CHAIN PROPAGATION AND TERMINATION

Subsequent stages in the oxidation of ethane thiol and methane thiol are believed to involve essentially the interaction with oxygen of ethyl and methyl radicals produced in reaction (6). The main oxidation products of ethyl radicals at 220°C are acetaldehyde and acetic acid; ¹⁶ these are also the principal products formed from ethane thiol in an oxygen-lean system (fig. 1). In the presence of more oxygen, further oxidation of acetaldehyde would be expected to occur and appreciable quantities of C_1 compounds are in fact produced (fig. 2).

In the same way, the oxidation products of methane thiol would be expected to include the oxidation products of the methyl radical. Carbon monoxide, formaldehyde and methanol are all formed when methyl radicals react with oxygen ^{32, 33} and in conformity with the results found for methane thiol (fig. 3 and 4), formaldehyde is generally less abundant than methanol. Methane formation is no doubt a further indication of the participation of methyl radicals.

The most probable mode of formation of disulphide is by radical recombination :

$$RS + RS \rightarrow RS . SR. \tag{7}$$

This reaction, which results in chain-termination, would take place most readily in oxygen-lean systems, and this may account for the inhibiting effect of both thiols on their own oxidation (table 2). The sulphur deficit noted in the intermediate stages of oxidation (fig. 4) may well be due to disulphide formation. Dimethyl disulphide is readily oxidized at 241° C³⁴ and in the presence of excess oxygen would undoubtedly be further attacked. No such deficit is observed in the oxidation of ethane thiol (fig. 2), possibly because any diethyl disulphide produced is oxidized very much more readily.³⁴ The failure to obtain direct evidence for the presence of disulphides in oxygen-lean systems may, however, be due to their strong adsorption on glass surfaces.³⁵

The authors would like to express their gratitude to the British Petroleum Company for the provision of a Research Studentship for one of us (L. C. R.) and for valuable financial assistance in the purchase of apparatus. They would also like to thank Mr. J. A. W. Dalziel for his help and advice.

- ² Schulze and Buell, Oil Gas J., 1935, 34, no. 21, 22.
- ³ Livingston, Ind. Eng. Chem., 1949, 41, 888.
- ⁴ Nelson and Buthod, in *Encyclopaedia of Chemical Technology*, vol. 10 (Interscience, New York, 1953), p. 143.
- ⁵ Meissner and Thompson, Trans. Faraday Soc., 1938, 34, 1238.
- ⁶ Skerrett and Thompson, Trans. Faraday Soc., 1941, 37, 81.
- ⁷ Sehon and Darwent, J. Amer. Chem. Soc., 1954, 76, 4806.
- ⁸ Boivin and Macdonald, Can. J. Chem., 1955, 33, 1281.
- ⁹ Thompson, Meyer and Ball, J. Amer. Chem. Soc., 1952, 74, 3284, 3287.
- ¹⁰ Feigl, Spot Tests in Organic Analysis (Elsevier Publishing Company, Amsterdam, 1956).
- ¹¹ Mapstone, J. Austral. Chem. Inst., 1948, 15, 236.

¹ Reid, in *Science of Petroleum* (ed. Dunstan *et al.*), vol. 2 (Oxford University Press, 1938), p. 1033.

- 12 Grant, Anal. Chem., 1947, 19, 345.
- 13 Goldman and Yagoda, Ind. Eng. Chem. (Anal.), 1943, 15, 377.
- 14 Georgia and Morales, Ind. Eng. Chem., 1926, 18, 305.
- ¹⁵ Boos, Anal. Chem., 1948, 20, 964.
- ¹⁶ Bell, Irish, Raley, Rust and Vaughan, Ind. Eng. Chem., 1949, 41, 2609.
- 17 Coope and Maingot, Anal. Chem., 1955, 27, 1478.
- 18 Cullis, Hinshelwood and Mulcahy, Proc. Roy. Soc. A, 1949, 196, 160.
- ¹⁹ Eastwood and Hinshelwood, J. Chem. Soc., 1952, 733.
- ²⁰ Bardwell, Proc. Roy. Soc. A, 1951, 207, 470.
- ²¹ Danby, Parsons and Hinshelwood, J. Chem. Soc., 1956, 1799.
- ²² Cullis and Isaac, Trans. Faraday Soc., 1952, 48, 1023.
- ²³ McDowell and Thomas, J. Chem. Soc., 1949, 2208, 2217.
- ²⁴ Newitt, Fifth Symposium on Combustion (Reinhold Publishing Corporation, New York, 1955), p. 558.
- ²⁵ Cullis, Bull. Soc. chim., 1953, 20, 777.
- ²⁶ Semenov, Chemical Kinetics and Chain Reactions (Oxford University Press, 1935), p. 288.
- ²⁷ Kerr and Trotman-Dickenson, J. Chem. Soc., 1957, 3322.
- 28 Birrell, Smith, Trotman-Dickenson and Wilkie, J. Chem. Soc., 1957, 2807.
- ²⁹ Barrett and Waters, Faraday Soc. Discussions, 1953, 14, 221.
- 30 Raley, Rust and Vaughan, J. Amer. Chem. Soc., 1948, 70, 88.
- ³¹ Rust, Seubold and Vaughan, J. Amer. Chem. Soc., 1950, 72, 338.
- ³² Bell, Raley, Rust, Seubold and Vaughan, Faraday Soc. Discussions, 1951, 10, 242.
- 33 Ingold and Bryce, J. Chem. Physics, 1956, 24, 360.
- ³⁴ Roselaar, unpublished work.
- 35 Coope and Bryce, Can. J. Chem., 1954, 32, 768.