

541. The Photodecomposition of Acetaldehyde Catalysed by Thiols.

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The photo-initiated thermal decomposition of acetaldehyde catalysed by alkanethiols and hydrogen sulphide has been investigated between 168° and 396°. The catalytic effect of the thiols is independent of their concentration over a limited range and is a function of the structure of the thiol so that the relative effects are : $\text{H}_2\text{S} > \text{MeSH} > \text{EtSH} > \text{Pr}^i\text{SH} > \text{Bu}^i\text{SH}$.

It is established that thiols react readily with free radicals. This finds application in the use of thiols as chain-transfer agents in free-radical polymerisation. However, very few kinetic studies of reactions involving thiols and $\text{RS}\cdot$ radicals have been reported. The only comprehensive study of thiol-catalysis appears to be that of Barrett and Waters,¹ on the catalysis of the decarbonylation of several saturated aliphatic aldehydes by alkanethiols in the liquid phase. The reaction chains were initiated by the thermal decomposition of dimethyl $\alpha\alpha'$ -azoisobutyrate and $\alpha\alpha'$ -azoisobutyronitrile. They supposed that the catalysis could be attributed to the supersession of the reaction (1')



by the faster cycle (2', 3')



The predominant chain-carrying step in the high-temperature photo-initiated decomposition of acetaldehyde in the vapour phase is almost certainly (1) :²



It appeared of interest to study the effect of adding thiols to the system, to see if reaction (1) would be superseded by the reactions equivalent to (2') and (3'). Experiments were therefore carried out with a number of thiols over a range of temperature. It was hoped that information would be obtained on the effect of structure on the reactivity of the thiols and on the relative rate constants of the reactions.

EXPERIMENTAL

Materials.—Acetaldehyde was prepared by distillation of paraldehyde containing a little sulphuric acid; it was thoroughly degassed before use, and stored as a gas in a blackened bulb. The hydrogen sulphide was generated in a Kipp's apparatus, dried, and degassed before use. The thiols were commercial samples; they were thoroughly degassed.

Apparatus.—The reactions were carried out in two very similar Pyrex reaction vessels, of about 200 c.c. each, placed side by side in an electric furnace with a quartz window. They were illuminated by the full light from a medium-pressure mercury arc which was allowed to warm for at least 20 min. before a run. The lamp was run continuously throughout a series of runs. Some runs with methanethiol were carried out with twin quartz cells. One of the cells was connected to a mercury manometer: the other to a di-*n*-butyl phthalate manometer for the measurement of the small quantities of thiol and to a Bourdon gauge with an optical lever for the measurement of the total pressure. When the cells were filled to the same pressure of pure acetaldehyde, the difference in the rates of photolysis was not significant. The cells, manometers, and storage bulbs were attached to a conventional vacuum-line.

Procedure.—A convenient pressure of thiol was admitted to one of the cells. Identical partial pressures of acetaldehyde were then admitted to both cells. The dead space was small, so that the measured pressures of reactants corresponded closely to the composition of the mixtures in the cells. After a few minutes (to allow the gases to come to the required temperature), light was admitted to the cells. The change in total pressure in each was then followed

¹ Barrett and Waters, *Discuss. Faraday Soc.*, 1953, **14**, 221.² Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, 2nd edn., 1954.

on a manometer. Measurements of the total pressures were made at conveniently spaced intervals.

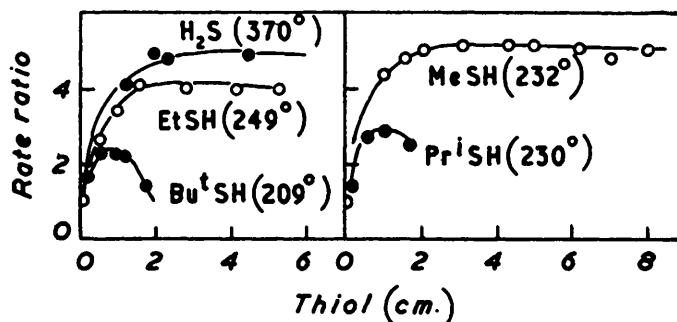
RESULTS AND DISCUSSION

It has been established by many workers that the products of the photo-initiated thermal decomposition of acetaldehyde are almost exclusively methane and carbon monoxide. In confirmation we found that the pressure in the vessel containing pure acetaldehyde approximately doubled when the run was carried to completion. The ultimate pressure increase in the vessel containing the thiol was always about 10% less than the initial partial pressure of acetaldehyde.

The catalytic effect of the thiol was determined from observations taken at the beginning of the reaction. The time taken for an increase in pressure equal to one-fifth of the initial pressure of acetaldehyde was measured for the catalysed and the uncatalysed system. It was found that substantially the same ratio was obtained if the initial slopes of the decomposition curves were measured or the ratios of the times taken to reach some other small degree of decomposition.

Most work was carried out with methanethiol as the catalyst. It was found that at a given temperature and pressure of acetaldehyde the catalytic effect of the thiol increased

FIG. 1. Typical variations of catalytic effect with concentration.



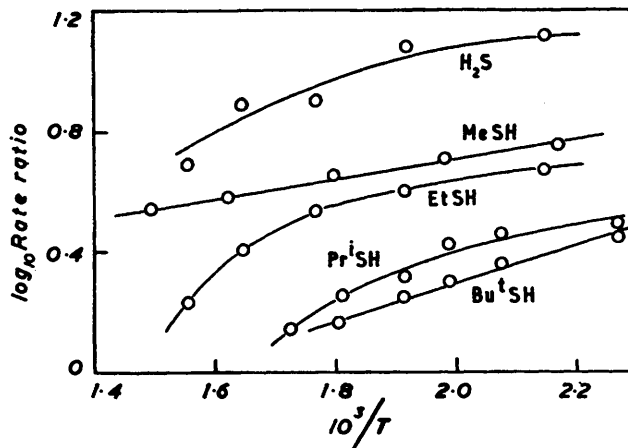
as its concentration was increased. Then the effect remained constant over a considerable range of concentration. Finally, when the thiol concentration was about three-quarters of the acetaldehyde concentration, the ratio increased at low light intensities. The variation of the ratio with concentration is shown in Fig. 1. All the points shown were obtained with an initial pressure of 10 cm. of acetaldehyde and with the same incident light intensity. It was found that in the concentration range represented by the flat portion of the curve no alteration in the ratio was brought about by doubling the aldehyde concentration or by varying the incident light intensity by a factor of four. The values of the constant rate ratios were determined at five temperatures between 189° and 396°. The values obtained have been plotted on the Arrhenius plot, Fig. 2.

Similar results were obtained from the experiments in quartz reaction vessels, though the rate ratios were always somewhat higher. It is likely that some reaction chains were initiated by the photolysis of the thiol by the unfiltered light from the mercury arc.

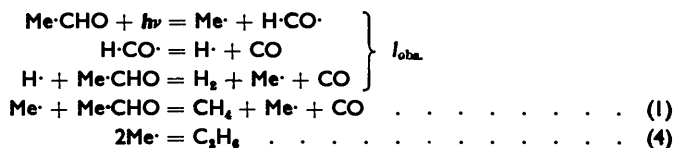
Similar experiments were carried out with each of the other thiols. Again it was found that for hydrogen sulphide and ethanethiol, the rate ratio increased with increasing thiol concentration until it reached a constant value (Fig. 1). With ethanethiol as catalyst the rate ratios were independent of a variation in absorbed light intensity by a factor of nine. The interpretation of the results with hydrogen sulphide is more uncertain. A slight induction period was evident at low light intensities and high concentrations of the sulphide. The rate ratios corresponding to the plateau are plotted against temperature for both catalysts in Fig. 2.

The catalytic behaviour of propane-2-thiol and 2-methylpropane-2-thiol is shown in Fig. 1. A constant rate ratio is never maintained over any considerable range of concentration, though the rate ratios are independent of a variation of light intensity by a factor of four. For purposes of comparison the maximum rate ratios for these catalysts are plotted against temperature in Fig. 2. At temperatures above 300° a small quantity of 2-methylpropane-2-thiol reduced the rate of the decomposition of acetaldehyde to negligible proportions. Propane-2-thiol behaved in the same manner at temperatures about 40° higher. There was no evidence that this inhibition was caused by products of the thermal decomposition of the thiols.

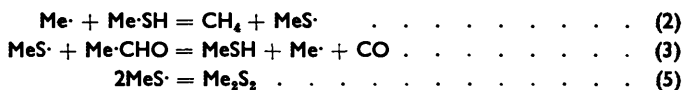
FIG. 2. Arrhenius plot for the catalytic effect of the thiols.



The mechanism of the photo-initiated thermal decomposition of acetaldehyde has often been written ² as :



It is now known that this is not a complete description, but it certainly represents the principal reactions correctly. A mechanism similar to that proposed by Barrett and Waters is adequate to cover the facts of the catalysis by methanethiol. The steps immediately consequent upon the absorption of light are followed by :



Disulphides have been found ¹ in the products of thiol-catalysed reactions at low temperatures, which supports the postulation of reaction 5.

The observed kinetics can only be simply explained on the assumption that the combination of RS· radicals is the chain-ending reaction. This reaction is very unlikely to have a greater rate constant than that for the combination of methyl radicals or the reaction of an RS· radical with a methyl radical. Consequently the steady-state concentration of RS· radicals must be much greater than that of methyl. This will only be so if *k*₂, the rate constant for reaction (2), is very much greater than *k*₁ or *k*₃. Unpublished results of Mr. J. A. Kerr in this Laboratory indicate that at low temperatures *k*₂ is at least fifty times *k*₁.

Solution of the steady-state equations yields (when the decomposition in the initiating step is neglected) :

$$-d[\text{Me}\cdot\text{CHO}]/dt = k_1(I_0/k_4)^{\frac{1}{2}}[\text{Me}\cdot\text{CHO}]$$

for the uncatalysed reaction, and :

$$-d[\text{Me}\cdot\text{CHO}]/dt = k_3(I_0/k_5)^{\frac{1}{2}}[\text{Me}\cdot\text{CHO}]$$

for the catalysed reaction.

$$\text{Rate ratio} = \frac{k_3(I_0/k_5)^{\frac{1}{2}}[\text{Me}\cdot\text{CHO}]}{k_1(I_0/k_4)^{\frac{1}{2}}[\text{Me}\cdot\text{CHO}]} = \frac{k_3 k_4^{\frac{1}{2}}}{k_1 k_5^{\frac{1}{2}}}$$

This equation should apply to the rate ratios in the region where they are independent of the thiol concentration. The rate ratio probably increases initially with thiol concentration because, at the lowest ratios, reaction (2) is not sufficiently faster than reaction (1).

Since k_1 and k_4 are known,^{3,4} $k_3/k_5^{\frac{1}{2}}$ can be evaluated. From the temperature coefficient of the rate ratio, $E_3 - E_1 - \frac{1}{2}E_5 + \frac{1}{2}E_4$ can be found where the E 's are the activation energies of the reactions.

Hence, assuming

$$\log_{10} k_1 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}\text{)} = 12.1 - (8400/2.303RT)$$

$$\log_{10} k_4 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}\text{)} = 13.3$$

we find $E_3 - \frac{1}{2}E_5 = 6800 \text{ cal. mole}^{-1}$.

Most combinations of small free radicals have very low activation energies and A factors of about $10^{13.3} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$.

Assuming $\log_{10} k_5 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}\text{)} = 13.3$ gives :

$$\log_{10} k_3 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}\text{)} = 11.9 - (6800/2.303RT)$$

This value of k_3 is probably reliable. The only cause for doubt is that the same simple mechanism will not describe the behaviour of the other thiols. However, the rate ratios with each of the catalysts were independent of their concentration over a detectable range, and also of the absorbed light intensity. These facts can only be readily interpreted on the assumption that reaction (2') represents the fate of virtually all the alkyl radicals released into the system. Therefore it seems probable that a mechanism substantially parallel to that for methanethiol holds for the other compounds, but that other side reactions must occur. In these circumstances it is impossible to derive rate constants for the elementary reactions. The rate ratio was found to reach its constant value for a lower concentration of methanethiol than for hydrogen sulphide. From such evidence the apparent order of reactivity for methyl radicals with the thiols (reaction 2') may be deduced :



This order is the opposite to that for the catalytic effect of the thiols ($k_3/k_5^{\frac{1}{2}}$). This is understandable: the first reaction would presumably be favoured by a weakening of the S-H bond, whereas the second would be favoured by its strengthening.

We are indebted to the British Petroleum Company for a grant in aid of this work.

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[Received, February 12th, 1957.]

³ Dodd, *Canad. J. Chem.*, 1955, **33**, 699.

⁴ Shepp, *J. Chem. Phys.*, 1956, **24**, 939.