# The Pyrolysis of Alkanethiols. Part 1. Kinetics of the Pyrolysis of Butane-1-thiol, Butane-2-thiol, and 2-Methylpropane-2-thiol

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The kinetics of the pyrolyses of the title alkanethiols into hydrogen sulphide and olefins have been studied in a static system in the temperature range 696.6—762.1 K and found, in the presence of cyclohexene, to be a homogeneous free radical process. For 2-methylpropane-2-thiol, the order of the reaction is 3/2 and the observed rate constant is expressible by the Arrhenius equation (i). For both butane-1- and -2-thiol, the order of the reaction is

$$^{3/2}k/\mathrm{cm}^{\frac{3}{2}}\ \mathrm{mol}^{-\frac{1}{2}}\ \mathrm{s}^{-1} = 10^{12.07 \pm 0.04} \exp(-169\ 800 \pm 600\ \mathrm{J\ mol}^{-1}/RT) \qquad \text{(i)}$$

1 and the rate constants are given by (ii) and (iii), respectively. A radical mechanism consistent with the results is proposed.

$$k/\mathrm{s}^{-1} = 10^{9.84 \pm 0.05} \exp(-178\ 100 \pm 800\ \mathrm{J\ mol}^{-1}/RT) \qquad \text{(ii)}$$

$$k/\mathrm{s}^{-1} = 10^{8.68 \pm 0.02} \exp(-174\ 600 \pm 300\ \mathrm{J\ mol}^{-1}/RT) \qquad \text{(iii)}$$

ALTHOUGH Arrhenius parameters, arising from a careful study of the kinetics of the olefin-yielding pyrolyses of many classes of alkyl derivatives, for example halides,[1] esters,[2] vinyl ethers,[3] *etc.* are well documented in the literature, such information is at present very scanty for alkanethiols. Except for a study of 2-methylpropane-2-thiol by Tsang[4] and partially of methane-, ethane-, and phenylmethane-thiols by Sehon and Darwent[5] the

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[1] A. Maccoll, *Adv. Phys. Org. Chem.*, 1965, **3**, 91.

[2] E. U. Emovon, *Nigerian J. Sci.*, 1969, **3**, 169.

[3] T. O. Bamkole, *J.C.S. Perkin II*, 1974, 801.

[4] Wing Tsang, *J. Chem. Phys.*, 1964, **40**, 1498.

[5] A. H. Sehon and B. de B. Darwent, *J. Amer. Chem. Soc.*, 1954, **76**, 4806.

existing reports[6-9] on alkanethiols tend to be qualitative and confusing as regards mechanism. Various mechanisms such as free radical, intramolecular α-elimination, and typical unimolecular four-centred, have been proposed. As some of these reports date rather far back, their qualitative nature may have stemmed from lack of adequate facilities for quantitative studies and it may be beneficial to up-date the reports in this direction.

The present study of the pyrolyses of alkanethiols seeks to remedy the above situation. Although activation parameters are reported by Tsang for 2-methylpropane-2-thiol, it was felt necessary to repeat the reaction of this compound in the static system that will be employed for the other compounds of the study. Since Thompson and Meyer[8] proposed an α-elimination mechanism for pentane-1-thiol, a situation allegedly encouraged by the presence of hydrogen atoms on the α-carbon atom, it was thought of interest to include some such systems in the study, hence the pyrolyses of butane-1- and -2-thiol were also included.

## RESULTS AND DISCUSSION

In the absence of cyclohexene, and in a vessel seasoned with allyl bromide, the pyrolyses under study exhibited an induction period followed by a fast reaction yielding the expected olefins, hydrogen sulphide, and a considerable amount of sulphur. When cyclohexene was added, the induction period, whose length increased with increasing partial pressure of cyclohexene persisted but the ensuing reaction did not result in obvious sulphur formation as when cyclohexene was absent. The kinetics reported are for the case when cyclohexene was present. For 2-methylpropane-2-thiol, the products were shown by g.l.c. to be essentially 2-methylpropene and hydrogen sulphide; for butane-1-thiol, the products were essentially but-1-ene and hydrogen sulphide while for butane-2-thiol, the products are a mixture of butenes and hydrogen sulphide. Using a Phasepak Q column, the mixture of hydrocarbon products was shown to be distributed as follows: but-1-ene *ca.* 17%, *cis*-but-2-ene *ca.* 38%, and *trans*-but-2-ene *ca.* 45%.

The reactions were followed by pressure measurement up to 20—30% reaction. The extent of reaction by this measurement coincided within experimental error with that determined by precipitation of the hydrogen sulphide as copper(II) sulphide. Beyond *ca.* 30% reaction and especially at the higher temperatures, pressure measurement showed higher rate of reaction due probably to side reactions of cyclohexene under this condition.

The orders of the reactions were determined by applying the initial rates method to the reaction immediately following at the end of the induction period and were found to be of order 3/2 in the thiol for 2-methylpropane-2-thiol and of order 1 in each thiol for butane-1- and -2-thiol. Consequently the first-order rate constants were calculated from a plot of log $M_t$ *versus* time $t$ where $M_t = 2P_o - (h + P_t)$ and $h$ is the pressure of added cyclohexene, $P_o$ is the total pressure initially and $P_t$ is the total pressure at any time $t$; while the 3/2 order rate constants, ${}^{3/2}k$ in pressure units (torr$^{-\frac{1}{2}}$ s$^{-1}$) were calculated from equation (1). The latter were then con-

$$ {}^{3/2}k = (2/M_t^{\frac{1}{2}}) - (2/M_o^{\frac{1}{2}}) \qquad (1) $$

verted to units of cm$^{3/2}$ mol$^{-\frac{1}{2}}$ s$^{-1}$ by multiplying by the appropriate factor, $(RT)^{\frac{1}{2}}$.

The homogeneity of the reactions was investigated by comparison of rates in a reactor packed with glass tubing ($S/V$ increased by more than 10-fold) with those in an unpacked reactor. The results obtained at 747.1 K are shown in Table 1. The lack of significant difference noted showed that the reactions are essentially homogeneous with possible wall termination of chains.

TABLE 1

| | Packed | Unpacked |
|---|---|---|
| Butane-1-thiol | | |
| $10^3k$/s$^{-1}$ | 2.14 | 2.46 |
| 2-Methylpropane-2-thiol | | |
| ${}^{3/2}k$/cm$^{3/2}$ mol$^{-1}$ s$^{-1}$ | 1.45 | 1.59 |

The temperature variations of the rate constants are shown in Table 2. The Arrhenius parameters resulting from these temperature variations are given in equations (2)—(4). In view of the earlier detailed product study by Thompson and Meyer,[8] it was not thought necessary to check in detail for the minor products of the reactions. The presence, under all conditions of an induction period which increased with increasing amount of cyclohexene added showed that the reactions being studied are radical processes.

butane-1-thiol

$$ k/\mathrm{s}^{-1} = 10^{9.84 \pm 0.05} \exp(-178\,100 \pm 800 \text{ J mol}^{-1}/RT) \qquad (2) $$

butane-2-thiol

$$ k/\mathrm{s}^{-1} = 10^{8.68 \pm 0.02} \exp(-174\,600 \pm 300 \text{ J mol}^{-1}/RT) \qquad (3) $$

2-methylpropane-2-thiol

$$ {}^{3/2}k/\mathrm{cm}^{3/2}\ \mathrm{mol}^{-\frac{1}{2}}\ \mathrm{s}^{-1} = 10^{12.07 \pm 0.04} \exp(-169\,800 \pm 600 \text{ J mol}^{-1}/RT) \qquad (4) $$

TABLE 2

Temperature variation of rate constants

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Butane-1-thiol | | | | | | | |
| $T$/K | 722.2 | 733.1 | 748.0 | 761.8 | | | |
| No. of runs | 5 | 4 | 5 | 6 | | | |
| $10^4k$/s$^{-1}$ | 9.08 | 14.58 | 25.08 | 42.41 | | | |
| Butane-2-thiol | | | | | | | |
| $T$/K | 715.0 | 725.1 | 735.7 | 742.3 | 750.1 | 756.4 | 762.1 |
| No. of runs | 7 | 5 | 5 | 8 | 5 | 7 | 3 |
| $10^4k$/s$^{-1}$ | 0.85 | 1.25 | 1.89 | 2.51 | 3.28 | 4.14 | 5.18 |
| 2-Methylpropane-2-thiol | | | | | | | |
| $T$/K | 696.6 | 708.0 | 715.9 | 724.5 | 734.8 | 745.2 | 749.0 |
| No. of runs | 6 | 8 | 7 | 6 | 6 | 9 | 6 |
| ${}^{3/2}k$/cm$^{3/2}$ mol$^{-\frac{1}{2}}$ s$^{-1}$ | 0.215 | 0.355 | 0.479 | 0.696 | 0.992 | 1.396 | 1.702 |

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[6] W. H. Malisoff and E. M. Marks, *Ind. and Eng. Chem.*, 1931, **23**, 114.

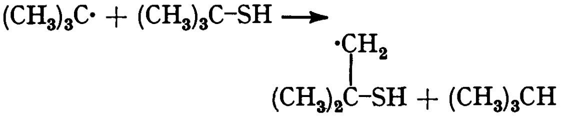
[7] M. R. Trenner and H. A. Taylor, *J. Chem. Phys.*, 1933, **1**, 77.

[8] C. J. Thompson, R. A. Meyer, and J. S. Ball, *J. Amer. Chem. Soc.*, 1952, **74**, 3284, 3287.

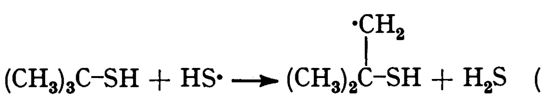
[9] J. L. Boivin and R. MacDonald, *Canad. J. Chem.*, 1955, **33**, 1281.

The 3/2 order reaction of 2-methylpropane-2-thiol is consistent with the mechanism put forward by Thompson and Meyer,[8] *viz.* equations (5)—(9). A steady state treatment of this mechanism and the assumption that the chains are long yields the rate law (10) from which

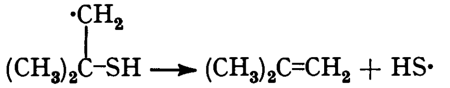
$$(CH_3)_3C{-}SH \longrightarrow (CH_3)_3C\cdot + HS\cdot \qquad (5)$$



$$(CH_3)_3C\cdot + (CH_3)_3C{-}SH \longrightarrow (CH_3)_2\overset{\cdot CH_2}{\overset{|}{C}}{-}SH + (CH_3)_3CH \qquad (6)$$



$$(CH_3)_3C{-}SH + HS\cdot \longrightarrow (CH_3)_2\overset{\cdot CH_2}{\overset{|}{C}}{-}SH + H_2S \qquad (7)$$



$$(CH_3)_2\overset{\cdot CH_2}{\overset{|}{C}}{-}SH \longrightarrow (CH_3)_2C{=}CH_2 + HS\cdot \qquad (8)$$

$$HS\cdot + HS\cdot \longrightarrow H_2S + S \qquad (9)$$

$$-d[(CH_3)_3CSH]/dt = k_7(k_5/k_9)^{\frac{1}{2}}[(CH_3)_3CSH]^{3/2} \qquad (10)$$

the observed rate constant $k_{obs} = k_7(k_5/k_9)^{\frac{1}{2}}$ and the observed activation energy $E_{obs} = E_7 + \frac{1}{2}(E_5 - E_9)$ where the numerical subscripts refer to the reaction.

An estimate of the activation energy $E_5$ for the first step of the mechanism can be made by use of thermochemical data. By combining data for the bond dissociation energies[10] for H–SH, H–C(CH$_3$)$_3$ and H–H with the heats of formation[11] of $H_2S$, $(CH_3)_3CH$, and $(CH_3)_3C{-}SH$, $E_5$ is estimated at 281 kJ mol$^{-1}$. Combining this with the activation energy in this study, and assuming that $E_9$ representing the activation energy for the combination of two radicals is approximately zero, $E_7$ is estimated at 29.3 kJ mol$^{-1}$.

The observed 3/2 order, the observed overall activation energy, and the reasonable pre-exponential factor seem to be in quantitative agreement with the mechanism of Thompson and Meyer. Tsang studied the pyrolysis of 2-methylpropane-2-thiol at much higher temperatures (930—1 230 K) than in this study, and the difference in mechanism may arise from this factor.

For the first order reactions of butane-1- and -2-thiol, the mechanism (11)—(15) is proposed. Application of the steady state assumption and the assumption of long chains involving •SH radicals give the rate law (16). By the thermochemical procedure, an estimate of $E_{11}$ as 297.4 for butane-1-thiol and 290.7 kJ mol$^{-1}$ for butane-2-thiol was obtained.

$$R{-}SH \longrightarrow R\cdot + HS\cdot \qquad (11)$$

$$R\cdot + RSH \longrightarrow RH + \cdot R'SH \qquad (12)$$

$$HS\cdot + RSH \longrightarrow \cdot R'SH + H_2S \qquad (13)$$

$$\cdot R'SH \longrightarrow \text{olefin} + HS\cdot \qquad (14)$$

$$\cdot SH + \cdot R'SH \longrightarrow R'(SH)_2 \longrightarrow \text{olefin} + H_2S + S \qquad (15)$$

$$-d[(RSH)]/dt = (k_{11}k_{13}k_{14}/k_{15})^{\frac{1}{2}}[RSH] \qquad (16)$$

It has been estimated earlier in this paper that the abstraction of hydrogen atoms by •SH radicals from 2-methylpropane-2-thiol requires *ca.* 29.3 kJ mol$^{-1}$. Assuming that the corresponding hydrogen abstractions from butane-1- and -2-thiol by •SH radicals require about the same activation energy, and assuming that $E_{15}$ corresponding to the combination of two radicals has a negligible value, then it is estimated that the self-dissociation of •R'SH to olefin and HS• requires not more than *ca.* 29.3 kJ mol$^{-1}$ for each thiol. While not wanting to attach too much importance to the absolute values of these estimates, they seem to be internally consistent.

It may be pertinent now to comment on three specific points, namely (i) the role of cyclohexene, (ii) the different orders noted, and (iii) the apparently low values of the pre-exponential factors for butane-1- and -2-thiols.

*The Role of Cyclohexene.*—As already noted, the presence of cyclohexene prevented the formation of an appreciable amount of sulphur compared with when it was absent. We consider two possible ways in which cyclohexene may serve to prevent formation of sulphur. (*a*) It may prevent the build-up of the concentration of •SH radical and thereby reduce the rate of steps (9) and (15). (*b*) Alternatively, there may be, besides the reactions represented by the 3/2 order and first-order schemes above, some other radical mechanism resulting in much sulphur formation which is much more sensitive to, and intercepted by, the presence of cyclohexene.

The pyrolyses reported were studied with cyclohexene : alkanethiol ratios of *ca.* 0.5—1.3 and over this range, there was no variation of rate constant with the ratio. If cyclohexene exerted its influence *via* the first method, a variation of rate constant with the cyclohexene : alkanethiol ratio would have been expected. Since this was not so, the second explanation for the role of cyclohexene looks more plausible.

Various authors, for example LeBel and DeBoer[12] and Challear and Dickson,[13] have shown that the photolysis of alkanethiols involves both R–S and S–H scissions. Therefore in pyrolysis carried out in the absence of cyclohexene, chains involving RS• and H• radicals, and presumably resulting in more copious sulphur formation, may be competing with those involving •SH radicals. The reaction has not been defined in this study.

The role of cyclohexene is presumably to trap these radicals, thus reducing sulphur formation leaving a residual reaction of the more predominant •SH radicals whose chains survive the presence of cyclohexene in the cyclohexene : thiol ratios employed in this study. A similar situation was reported by Challear and Dickson[13] where it was found that photolysed methanethiol showed

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[10] M. F. R. Mulcahy, 'Gas Kinetics,' Nelson, London, 1973, p. 117.

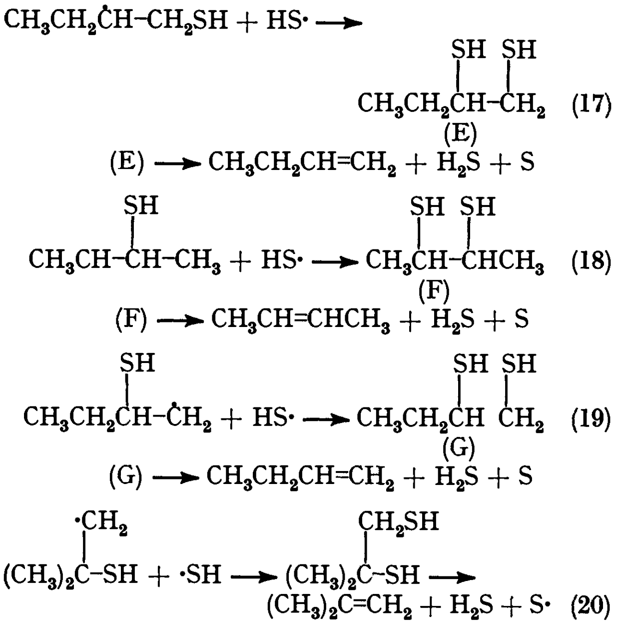
[11] D. R. Stull, E. F. Westrum, and G. C. Sinke, 'Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969, pp. 685, 245, and 615.

[12] N. A. LeBel and A. DeBoer, *Mechanisms React. Sulphur Compounds*, 1968, **3**, 99.

[13] A. B. Challear and D. R. Dickson, *Trans. Faraday Soc.*, 1970, **66**, 1987.

the spectrum of $S_2$ but that when photolysed in the presence of ethene, the $S_2$ spectrum was completely suppressed.

*Orders of Reactions.*—One has to propose a cross-termination of radicals to explain the first-order reactions of butane-1- and -2-thiols. For butane-1-thiol, this is reaction (17) while for butane-2-thiol, it is either (18) or (19). A corresponding cross-termination step, not supported for 2-methylpropane-2-thiol is (20).



$$\mathrm{CH_3CH_2\dot{C}H{-}CH_2SH + HS\cdot \longrightarrow \underset{(E)}{CH_3CH_2\overset{SH}{\overset{|}{C}}H{-}\overset{SH}{\overset{|}{C}}H_2}} \quad (17)$$

$$\mathrm{(E) \longrightarrow CH_3CH_2CH{=}CH_2 + H_2S + S}$$

$$\mathrm{CH_3CH{-}\overset{SH}{\overset{|}{C}}H{-}CH_3 + HS\cdot \longrightarrow \underset{(F)}{CH_3\overset{SH}{\overset{|}{C}}H{-}\overset{SH}{\overset{|}{C}}HCH_3}} \quad (18)$$

$$\mathrm{(F) \longrightarrow CH_3CH{=}CHCH_3 + H_2S + S}$$

$$\mathrm{CH_3CH_2\overset{SH}{\overset{|}{C}}H{-}\dot{C}H_2 + HS\cdot \longrightarrow \underset{(G)}{CH_3CH_2\overset{SH}{\overset{|}{C}}H\ \overset{SH}{\overset{|}{C}}H_2}} \quad (19)$$

$$\mathrm{(G) \longrightarrow CH_3CH_2CH{=}CH_2 + H_2S + S}$$

$$\mathrm{(CH_3)_2\overset{\cdot CH_2}{\overset{|}{C}}{-}SH + \cdot SH \longrightarrow (CH_3)_2\overset{CH_2SH}{\overset{|}{C}}{-}SH \longrightarrow (CH_3)_2C{=}CH_2 + H_2S + S\cdot} \quad (20)$$

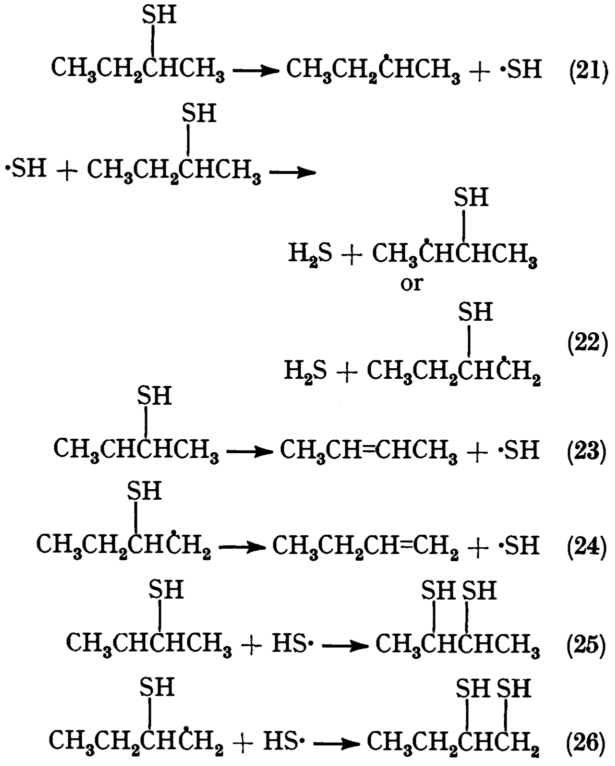
Looking at the alkyl radicals in these termination steps, for steps (17) and 18), they are secondary radicals whereas for (19) and (20), they are primary. The former are known to be thermodynamically more stable than the latter. The fact that butane-1- and -2-thiol are cross-terminated whereas 2-methylpropane-2-thiol involving only a primary alkyl radical is not, is a reflection of this thermodynamic stability.

Although the tertiary radical $(CH_3)_3C\cdot$ will, by this token, be more stable, its involvement will not be kinetically significant as it is not involved in the chain propagating steps.

*Low Pre-exponential Factors.*—Following the procedure of O'Neal and Benson,[14] some of the contributions to the entropy changes that occur in the formation of the transition state will come from changes in translational motions, electronic degeneracy, symmetry, vibrational motions, and internal rotations. Out of these factors, symmetry changes look particularly relevant to the present problem.

The contribution to entropy changes arising from symmetry considerations is $R\ln(\sigma\eta^*/\eta\sigma^*)$ where $\sigma$ and $\sigma^*$ are the overall symmetry numbers of the ground state and the activated complex respectively and $\eta$ and $\eta^*$ are the numbers of optical isomers of the ground and transition states respectively.

For butane-2-thiol, the detailed scheme is (21)—(26). The contribution from this consideration is $-R\ln 2$ (*i.e. ca.* $-1.38$ cal mol$^{-1}$ K$^{-1}$) for each of steps (21), (23), and (24) while it is $+R\ln 2$ for step (26). The observed pre-exponential factor $A_{\mathrm{obs}} = (A_{21}A_{22}A_{24}/A_{26})^{\frac{1}{2}}$. Assuming that the observed pre-exponential factor for 2-methylpropane-2-thiol is normal, then $A_{\mathrm{obs}}$ for butane-2-thiol will be significantly less than normal since both $A_{21}$ and $A_{24}$ have decreased while $A_{26}$ has increased. When a corresponding scheme is applied to butane-1-thiol, only steps (25) and (26) result in the creation of an asymmetric centre, thus resulting in an increase of $A_{26}$.



$$\mathrm{CH_3CH_2\overset{SH}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CH_2\dot{C}HCH_3 + \cdot SH} \quad (21)$$

$$\mathrm{\cdot SH + CH_3CH_2\overset{SH}{\overset{|}{C}}HCH_3 \longrightarrow H_2S + CH_3\dot{C}H\overset{SH}{\overset{|}{C}}HCH_3 \text{ or } H_2S + CH_3CH_2\overset{SH}{\overset{|}{C}}H\dot{C}H_2} \quad (22)$$

$$\mathrm{CH_3CH\overset{SH}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CH{=}CHCH_3 + \cdot SH} \quad (23)$$

$$\mathrm{CH_3CH_2\overset{SH}{\overset{|}{C}}H\dot{C}H_2 \longrightarrow CH_3CH_2CH{=}CH_2 + \cdot SH} \quad (24)$$

$$\mathrm{CH_3CH\overset{SH}{\overset{|}{C}}HCH_3 + HS\cdot \longrightarrow CH_3\overset{SH}{\overset{|}{C}}H\overset{SH}{\overset{|}{C}}HCH_3} \quad (25)$$

$$\mathrm{CH_3CH_2\overset{SH}{\overset{|}{C}}H\dot{C}H_2 + HS\cdot \longrightarrow CH_3CH_2\overset{SH}{\overset{|}{C}}H\overset{SH}{\overset{|}{C}}H_2} \quad (26)$$

Thus the overall pre-exponential factor for butane-1-thiol shall also be less than normal but greater than for butane-2-thiol. The result obtained is in qualitative agreement with this expectation.

## EXPERIMENTAL

2-Methylpropane-2-thiol (B.D.H.) and butane-2-thiol (B.D.H.) were fractionated. The fractions with b.p. 63.5—64 °C (lit.,[15] 63.8—64.2 °C) and 84 °C (lit.,[15] 84—85 °C), respectively, were used. Butane-1-thiol was prepared by the method of Vogel.[16] The fraction with b.p. 97—98 °C (lit.,[16] 97—99 °C) was used. Cyclohexene (B.D.H.) was treated with sodium sulphite, dried, and distilled. The fraction with b.p. 83 °C was used in this work. The purity of these compounds was determined by g.l.c. and was found to be over 99% in each case.

The apparatus used was a conventional static system coupled to a Mitronic Micro-comparator and a Smith's

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[14] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1967, **71**, 2903.

[15] I. Helbron, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, p. 2311.

[16] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longman, London, 1968, p. 497.

Servoscribe potentiometric recorder for automatic recording of pressure variation in the reaction vessel. The vessel was embedded in an electrically heated aluminium block and its temperature was controlled by a Versicon type 101 temperature controller to within ±0.2 K. The reactions were carried out by distilling the reactants (known pressures of cyclohexene and the appropriate alkanethiol) into the vessel which had been previously seasoned with the products of the decomposition of allyl bromide and recording the pressure variation automatically over the first 30% or more of the reaction.

The products of decomposition were analysed by g.l.c. The amount of hydrogen sulphide produced was determined by precipitation of copper sulphide from a standard acid solution of copper sulphate.

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