Gase-phase Thermolysis of Sulphur Compounds. Part I. Di-t-butyl Disulphide

By **G. Martin** * and **N. Barroeta**, Centre of Petroleum and Chemistry, Instituto Venezolano de Investigaciones Cientificas, Apartado 1827, Caracas, Venezuela

The gas-phase thermolysis of di-t-butyl disulphide was studied in a stirred-flow system using the toluene carrier technique in the temperature range 330—400 °C. The temperature dependence of the rate coefficients is given by the equation log k = 14.6 ± 0.4 − (184 ± 4) kJ mol^{-1}/2.303RT. In a static system, the Arrhenius equation obtained was log k = 13.6 ± 0.2 − (177 ± 2) kJ mol^{-1}/2.303RT in the temperature range 246—300 °C and initial pressures between 60 and 212 Torr. In both cases the kinetics followed a first-order law. The reaction products were mainly isobutene and hydrogen disulphide, the latter decomposing partially into sulphur and hydrogen sulphide on the surface of the glass. 5 mole % isobutane was found in the hydrocarbon product throughout the whole temperature range, and it was as high as 13% when the static system was used. A unimolecular mechanism for the decomposition is proposed in which isobutene and hydrogen t-butyl disulphide are formed in the first step, the latter decomposing rapidly into hydrogen disulphide and isobutene in the second step.

THE literature on the thermal decomposition of thiols, sulphides, and disulphides shows that kinetic data concerning this important reaction are scarce. Only a few thiols [1-5] and sulphides [6,7] have so far been studied, some under ill defined experimental conditions which render the results unsuitable for quantitative evaluations.

Recently, Emovon and Bamkole [5] studied the gas phase thermolysis of n-, s-, and t-butyl thiol in a static system and found that the uninhibited reaction proceeds essentially by a free radical mechanism. For the cyclohexene inhibited reaction they reported the Arrhenius equations (1)—(3)

$$\text{n-butyl} : \log k = 15.75 - (260.4 \text{ kJ mol}^{-1}/2.3RT) \quad (1)$$

$$\text{s-butyl} : \log k = 14.65 - (243.3 \text{ kJ mol}^{-1}/2.3RT) \quad (2)$$

$$\text{t-butyl} : \log k = 13.4 \; - (227.2 \text{ kJ mol}^{-1}/2.3RT) \quad (3)$$

The frequency factors for n- and s-butyl thiol are too high for a concerted process; however, it is concluded [5] that the decomposition is 'generally unimolecular'. The results [5] on t-butyl thiol agree well with those of Wing Tsang [3] who studied the reaction in a shock tube.

In regard to organic sulphides, only methyl phenyl and benzyl methyl sulphide have been studied kinetically. For the first, Back and Sehon [6] reported the Arrhenius equation $k/\text{s}^{-1} = 3 \times 10^{14} \exp(-251.0 \text{ kJ mol}^{-1}/RT)$ $^{-1}$. For benzyl methyl sulphide Braye et al.[7] reported log k = 13.48 − (215 ± 8)kJ mol^{-1}/2.3RT). In both cases the toluene carrier technique was used and the activation energies were identified with $D(\text{C}_6\text{H}_5\text{S–CH}_3)$ and $D(\text{C}_6\text{H}_5\text{-CH}_2\text{-SCH}_3)$ respectively.

Coope and Bryce [8] studied the thermolysis of dimethyl disulphide in a static system and found that for this compound the primary reaction was the formation of methyl thiol and a thioformaldehyde polymer. They reported an activation energy of 188 ± 17 kJ mol^{-1} and a frequency factor of 2×10^{13} s^{-1} for the overall reaction.

These sulphur compounds are present in varying amounts in crude oils and although they can be easily separated by simple distillation, they can undergo thermal reactions during processing with the appearance of new compounds both in the distillate and the residues. It is therefore important to investigate their thermolyses keeping in mind the relation and possible application to direct desulphurization methods.

RESULTS

Stoicheiometry and Product Distribution.—Dynamic method. Table 1 presents a sample of the analytical data from a total of 50 runs carried out in the stirred-flow system over the temperature range 400—330 °C.

Isobutene and hydrogen disulphide were the main products of decomposition. 5 Mole % isobutane was also detected throughout the temperature range in the hydrocarbon products. Some hydrogen sulphide resulted from thermal decomposition of H_2S_2; however, we believe that the largest part was formed outside the quartz reaction vessel when H_2S_2 was in contact with the Pyrex glass surfaces. The increased amount of H_2S formed when CO_2 is used as carrier gas is due to the fact that in these runs H_2S_2 is more exposed to the glass surfaces during the fractionation of the products. A mass spectral analysis of a yellow solid accumulated in the first trap showed it to be elemental sulphur. This sulphur was not quantitatively measured. The use of cyclohexene as carrier gas in two runs did not cause any variation either in product distribution or value of the rate coefficient. Since toluene is an inhibitor of radical chain reactions, we did not consider it necessary to carry out more runs with cyclohexene as carrier gas especially in view of the fact that this substance had no effect on rate in the static system.

The order of the reaction for the disappearance of disulphide was found to be 0.99 ± 0.03 at 350 °C. This figure was obtained by a least-squares linear fit of data (Figure 1). A reaction order of one was assumed *a priori* and the rate coefficients were calculated using Mulcahy and

[1] H. A. Taylor and E. T. Layng, *J. Chem. Phys.*, 1933, **1**, 798.
[2] A. H. Sehon and B. Darwent, *J. Amer. Chem. Soc.*, 1954, **76**, 4806.
[3] Wing Tsang, *J. Chem. Phys.*, 1964, **40**, 1968.
[4] C. J. Thompson, R. A. Meyer, and J. S. Ball, *J. Amer. Chem. Soc.*, 1952, **74**, 3284.

[5] E. U. Emovon and T. O. Bamkole, 3rd Internat. Symposium on Gas Kinetics, Brussels, 1973.
[6] M. H. Back and A. H. Sehon, *Canad. J. Chem.*, 1960, **38**, 1076.
[7] E. H. Braye, A. H. Sehon, and B. Darwent, *J. Amer. Chem. Soc.*, 1955, **77**, 5282.
[8] J. A. R. Coope and W. A. Bryce, *Canad. J. Chem.*, 1954, **32**, 768.

TABLE 1

Thermolysis of di-t-butyl disulphide in the stirred-flow system

T/°C	10^8 Flow rate (mol s^{-1})			P/Torr	10^4 Product (mol)				k/s^{-1}	%r [f]
	f_c [a]	f_s^0 [b]	f_p [c]		RSSR [d]	C_4 [e]	H_2S_2	H_2S		
400.4	7 974	84	137	8.28	5.78	15.8	5.92	1.97	1.732	53
388.8	6 574	595	699	7.54	38.6	81.4	33.3	7.39	0.969 3	38
371.0 *	5 125	428	290	6.42	12.4	25.4	4.22	(8.14) ‡	0.355 6	20
369.0	6 127	623	462	10.1	27.0	55.2	22.9	5.16	0.320 4	24
358.8	4 621	466	285	11.3	16.4	32.6	14.6	2.74	0.168 5	20
358.5 *	4 164	349	248	9.69	11.8	24.1	3.73	(8.30) ‡	0.194 8	21
361.7 †	1 473	203	340	13.4	19.4	39.4	12.2	10.5	0.199 9	48
350.1	2 198	108	92	10.1	6.15	12.6	5.01	1.49	0.123 8	26
339.0	1 547	198	126	12.1	10.4	20.0	7.25	2.48	0.059 1	21
328.2	2 446	389	93	11.6	4.67	12.4	5.58	1.36	0.030 0	8

* CO$_2$ as carrier gas. † Cyclohexene as carrier gas. ‡ Estimated amount.

[a] Inflow rate of carrier gas (toluene). [b] Inflow rate of reactant. [c] Total outflow rate of products. [d] Amount of decomposed sulphide = total input of reactant − amount of unchanged reactant in effluent. [e] Total hydrocarbon product (mol). [f] % Reactions.

Williams'[9] complete equation with the stoicheiometric factor x measured at each run.
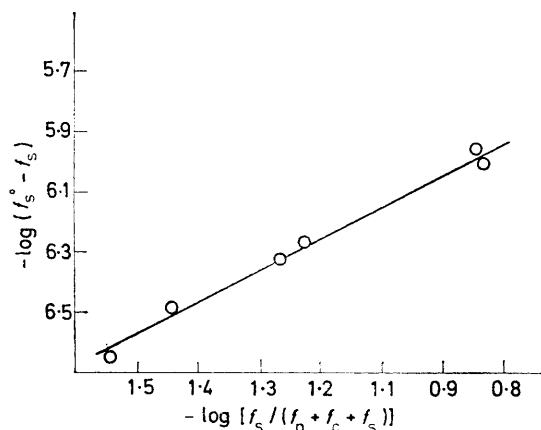
Static method. We were able to study the pyrolysis of

FIGURE 1 Order of reaction for disappearance of di-t-butyl disulphide at 350 °C

the disulphide between 246 and 300 °C by this technique. As shown in Table 2, ΔP values are a valid measure of the extent of reaction and further the reaction is accompanied

TABLE 2

Stoicheiometry of the thermolysis of di-t-butyl disulphide in the static system

T/°C	P_0/Torr	P_t/P_0	%r [a] from pressure measurement	%r [a] from hydrocarbon produced
280	100		49.7	48.2
280	96	3.03		
280	139		71.3	65.0
280	184		48.4	49.8
280	60		70.0	68.8
280	79		50.3	48.5
289	212		44.6	47.1
294	49	3.02		
294	137	2.97		
299	152	3.15		

[a] % Reactions.

by a three-fold pressure increase. Accordingly the first-order integrated equation for a 1 ⟶ 3 stoicheiometry was tried and found to reproduce the pressure–time curve up to

[9] M. F. R. Mulcahy and D. J. Williams, *Austral. J. Chem.*, 1961, **14**, 534.

90% conversion for initial pressures in the range 60—212 Torr. A detailed product analysis for two runs at 280 °C is shown in Table 3.

Quantitative analysis for the C_4 hydrocarbons, which is made up of 87% of isobutene and 13% isobutane, implies a 1 : 1 correlation with the percentage of reaction as measured by the total pressure increase. The sulphur analysis, on the other hand, invariably gave about half the value expected from the latter but this was due to the fact that

TABLE 3

Product analysis for thermolysis of di-t-butyl disulphide at 280 °C

(A) $P_0 = 79.0$ Torr (5.71×10^{-4} mol), $P_t = 158.5$ Torr (50% reaction)

Product	10^4 mole		10^4 mole	
			Calc.	Meas.
H_2S	3.16	C	22.8	22.2
Isobutene	4.60	H	51.4	52.5
Isobutane	0.94	S	5.7	3.2

(B) $P_0 = 102$ Torr (7.37×10^{-4} mole), $P_t = 306$ Torr (100% reaction)

Product	10^4 mole		10^4 mole	
			Calc.	Meas.
H_2S	7.97	C	58.9	43.8
Isobutene	9.08	H	132.7	107.2
Isobutane	1.86	S	14.7	7.8

H_2S_2 decomposed into H_2S and S during the manipulation in the vacuum line prior to analysis. In fact, when the yellowish material that accumulated inside the glass tubing was subject to mass spectral analysis it was shown to be mainly sulphur, although some material of formula $C_4H_4S_3$ was also detected.

It was clearly demonstrated that the value of the first-order rate constants could not be modified significantly by the addition of cyclohexene in concentrations as high as 140% relative to the reactant or by increasing the surface : volume ratio of the reaction vessel by a factor of five. However, for the runs carried out in the presence of cyclohexene the concentration of isobutane rose to 26% of total hydrocarbon.

DISCUSSION

The above results, especially those of the stirred-flow system clearly indicate that the decomposition of di-t-butyl disulphide takes place according to the overall process (4). The low number of primary reaction

$$Bu^tS\text{–}SBu^t \longrightarrow H_2S_2 + 2CH_2\text{=}CMe_2 \qquad (4)$$
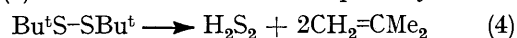
products and the smooth pressure–time curves, with no indication of an induction period, obtained in the static experiments suggest that complex free radical chain processes do not take place to any large extent. The formation of hydrogen disulphide can be readily explained by means of a two step molecular mechanism *via* four centred transition states as represented in Figure 2.
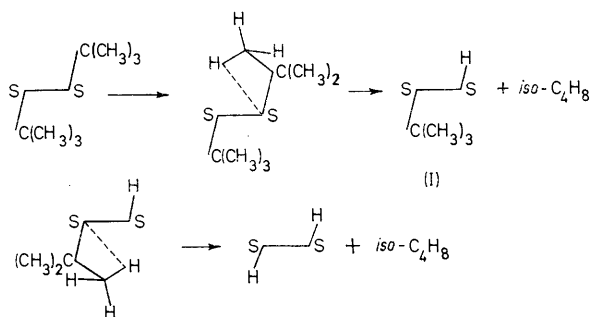
According to this scheme, hydrogen t-butyl disulphide (I) is produced first, decomposing rapidly into hydrogen disulphide and a second molecule of isobutene. This mechanism is more feasible than a simultaneous concerted elimination of two molecules of isobutene, evidence in this connection being the appearance of a peak of m/e 122 in the mass spectrum of the pure disulphide which corresponds to compound (I).

TABLE 4

Arrhenius parameters for the thermolysis of di-t-butyl disulphide

	$\log_{10}(A/\text{s}^{-1})$	$E_a/\text{kJ mol}^{-1}$	$T/^{\circ}\text{C}$
Static	13.57 ± 0.22	177 ± 2	246—300
Flow	14.6 ± 0.4	184 ± 4	328—400
Combined results	15.98 ± 0.55	201 ± 4	257—389

Table 4 gives the Arrhenius parameters obtained by a 95% confidence limit least-square linear fit of the experimental rate coefficients and Figure 3 shows the corresponding Arrhenius plots. The frequency factor for the reaction in the flow system seems unexpectedly high for a four-centred unimolecular reaction. On the other hand, the static experiments yield $\Delta S^{\ddagger}$ of nearly zero at 633 K. The contribution to $\Delta S^{\ddagger}$ from 18 equivalent hydrogen atoms is more than offset by the loss of two large internal rotations in the transition state and hence the value of the frequency factor for this reaction can be expected to have an upper limit of $10^{13.6}$ s^{-1}, the same as that calculated by Benson and O'Neal [10] for t-butyl thiol. Considering that flow measurements are subject to more experimental error than static ones, we believe that the Arrhenius parameters derived from the latter are more representative of

the unimolecular process. The fact that the results obtained by the two techniques do not differ significantly supports the idea of the same basic mechanism operating in both cases. Accepting that the thermolysis of di-t-butyl disulphide takes place primarily through a molecular process, it only remains to explain the origin of the 5—13% isobutane formed in the reaction. The most plausible explanation would be the formation of t-butyl radicals by simple fission of a C-2 bond, these t-butyl radicals then disproportionating to form one molecule each of isobutene and isobutane. The increased proportion of isobutane when the reaction took place in the presence of cyclohexene can be explained by the fact that abstraction of hydrogen from the latter competes favourably with disproportionation of t-butyl radicals. The reported values [11] for both D(S–C) and D(S–S) are
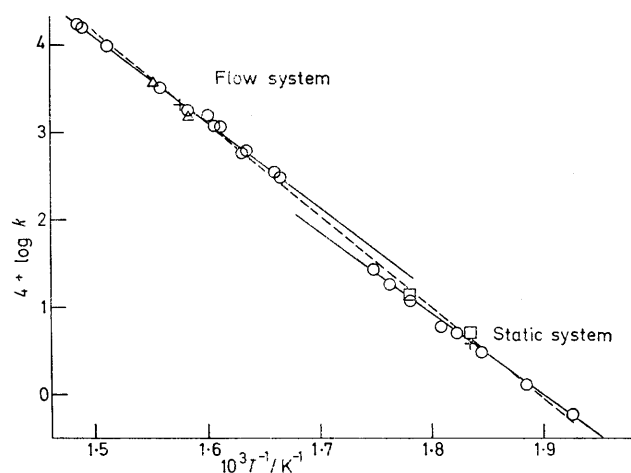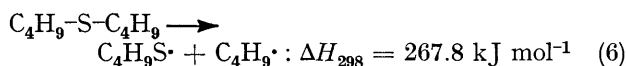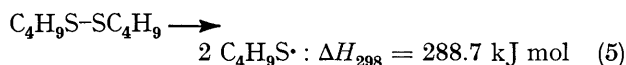

FIGURE 3　Arrhenius plots: $+$, in presence of cyclohexene; $\triangle$, in presence of CO_2; $\square$, packed vessel

within the range 285—305 kJ mol^{-1} and for the particular case of t-butyl sulphide and disulphide one can obtain using Benson and O'Neal's [12] values the enthalpy changes for reactions (5) and (6). According to these

$$C_4H_9S\text{–}SC_4H_9 \longrightarrow$$
$$2\ C_4H_9S\cdot : \Delta H_{298} = 288.7 \text{ kJ mol} \quad (5)$$

$$C_4H_9\text{–}S\text{–}C_4H_9 \longrightarrow$$
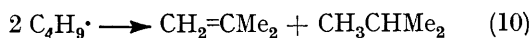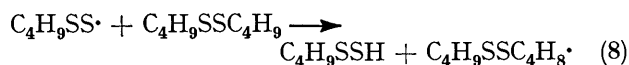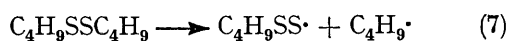$$C_4H_9S\cdot + C_4H_9\cdot : \Delta H_{298} = 267.8 \text{ kJ mol}^{-1} \quad (6)$$

figures, C–S bond fission requires less energy; however, these quantities have an uncertainty of at least ± 18 kJ mol^{-1} which makes difficult a clear decision on which bond is likely to break first. We have obtained a value of 272 ± 4 kJ mol^{-1} for the activation energy of the t-butyl sulphide decomposition in the presence of cyclohexene. As will be explained in Part II, that value is identified with the C–S bond dissociation energy in agreement with the above estimate. The reaction products we observe for the disulphide are difficult to reconcile with an initial breaking of the S–S bond, a fact

[10] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1967, **71**, 2903.
[11] T. L. Cottrell, ' The Strength of Chemical Bonds,' Academic Press, New York, 1954.

[12] H. E. O'Neal and S. W. Benson, *Free Radicals*, 1973, **2**, 338.

which is in line with the general observation [13] that di-sulphides do not lead to the production of RS· radicals easily on thermolysis and give support to the value listed by Cotrell.[11] Again, the absence of a significant peak at m/e 89 in the mass spectrum of the pure disul-phide is suggestive of the C–S bond being weaker than the S–S one. In any case, the magnitude of the experi-mental activation energy rules out any mechanism whose rate-determining step is the breaking of the S–S bond.

The fate of the radical C_4H_9SS· would be the abstrac-tion of a hydrogen atom from a molecule of material with the onset of the short chain process (7)—(10).

$$C_4H_9SSC_4H_9 \longrightarrow C_4H_9SS\cdot + C_4H_9\cdot \qquad (7)$$

$$C_4H_9SS\cdot + C_4H_9SSC_4H_9 \longrightarrow$$
$$C_4H_9SSH + C_4H_9SSC_4H_8\cdot \qquad (8)$$

$$C_4H_9SSC_4H_8\cdot \longrightarrow C_4H_9SS\cdot + CH_2{=}CMe_2 \qquad (9)$$

$$2\,C_4H_9\cdot \longrightarrow CH_2{=}CMe_2 + CH_3CHMe_2 \qquad (10)$$

The reduced amount of isobutane formed in the flow experiments could be explained if one considers the much shorter reaction time which considerably reduces com-plications due to secondary reactions. At present we are studying the thermolysis of unsymmetrical disul-phides in order to find evidence for a contribution from a radical process.

[13] J. L. Kice, ref. 12, p. 711.
[14] K. H. Butler and O. Maass, *J. Amer. Chem. Soc.*, 1930, **52**, 2184.

EXPERIMENTAL

Di-t-butyl disulphide was obtained from Aldrich Chemical Co. A batch was prepared by oxidation of t-butyl thiol with iodine. The purity was checked periodically by g.l.c. (5 ft × 8 in O.D. 3% SE30 on 100/120 mesh Varaport 30 at 90 °C) and found to be $\geqslant 98\%$. The hydrocarbon products were analysed on a 6 ft × 8 in O.D. column packed with 80—100 mesh Porapak R with 3% Nujol at 100 °C. Helium was always used as carrier gas.

A sample of hydrogen disulphide was prepared following the method of Butler and Maass.[14] This product was quantitatively measured by trapping the liquid effluent at −78 °C and adding to it a measured excess of 0.2M-silver nitrate solution in 80% ethanol–water. The C_4 hydro-carbons, together with the H_2S were collected at −190 °C in a measured amount of the $AgNO_3$ solution which trapped the H_2S. The hydrocarbons were then pumped out through a trap cooled at −78 °C and collected in a calibrated gas burette. The vacuum flow system and experimental technique were similar to that described by Mulcahy and Williams.[9] The order of the reaction was determined by a method similar to that described by Graaf and Kwart.[15] Static experiments were carried out in a conventional vacuum system using a glass mirror gauge [16] to follow the pressure increase manometrically. A Varian Mat 111 g.l.c.–m.s. system was used for product identification.

[15] J. de Graaf and H. Kwart, *J. Phys. Chem.*, 1963, **14**, 534.
[16] A. Maccoll, *Chem. Rev.*, 1969, **69**, 33.