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### GAS-PHASE THERMOLYSIS OF DITERTIARY BUTYL SULPHIDE AND 1-PROPENYL TERT-BUTYL SULPHIDE

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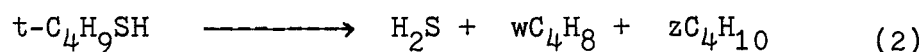
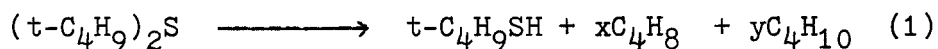
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# GAS-PHASE THERMOLYSIS OF DITERTIARY BUTYL SULPHIDE AND 1-PROPENYL tert-BUTYL SULPHIDE.

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In this work we have studied the pyrolysis of ditertiary butyl sulphide (TBS) and the asymmetrical 1-propenyl tert-butyl sulphide (PTS) both in static and stirred-flow systems. TBS was pyrolyzed in the temperature range 330-410°C in the static system and between 467-443°C in the flow system. In the former, the ratio final pressure/initial pressure (Pf/Po) had a value of  $1.9 \pm 0.23$  when the reaction was made in the presence of 50% of cyclohexene as free radical chain inhibitor. In absence of cyclohexene, the ratio Pf/Po had a value of  $2.8 \pm 0.12$ . The stoichiometry of the reaction in absence of any additive can be represented by the equations



$$y/x = z/w = 0.30 \quad x+y = 1 \quad z+w = 1$$

The second process is practically suppressed by the addition of cyclohexene. Under these conditions, the reaction showed a first order kinetics with the rate coefficients following the Arrhenius equation

$$\log k = (17.6 \pm 0.4) - (260 \pm 5) \text{kJmol}^{-1} / 2.3RT$$

between 365 and 467°C. Below 365°C the Arrhenius plot showed an abrupt change of slope suggesting a heterogeneous reaction predominating under these conditions.

It is proposed that at temperatures above 365°C and in the presence of 50% cyclohexene the mechanism is a free radical non chain process where the activation energy is a measure of the C-S bond dissociation energy.

The results obtained in the pyrolysis of PTS indicate that it decomposes about ten times faster than TBS and the reaction

is not inhibited by cyclohexene in amounts up to 60%. The ratio  $P_f/P_o$  always reached a value of 2.0, however, the quantitative analysis of the products indicated that most of the  $\text{CH}_3\text{-CH=CH-S}$  moiety of the starting molecule polymerizes outside the reactor to the trimer  $\text{C}_9\text{H}_{18}\text{S}_3$  while the tert-butyl moiety is quantitatively found as 80% isobutylene plus 20% isobutane.

A first order rate equation applies up to 80% reaction, as measured by pressure increase, glc measurement of the unreacted material and the measurement of the  $\text{C}_4$  hydrocarbon product. In the temperature range 340-387°C the rate coefficients follow the Arrhenius equation

$$\log k = (13.43 \pm 0.05) - (199 \pm 0.6) \text{kJmol}^{-1} / 2.3RT$$

which is suggestive of a molecular process.