

THE REACTION OF THIOLANE WITH HYDROGEN ATOMS IN GAS PHASE

Osamu HORIE, Kazunori KAWAMATA, Kaoru ONUKI, and Akira AMANO  
Department of Applied Chemistry, Faculty of Engineering,  
Tohoku University, Aoba, Aramaki, Sendai 980

The title reaction was carried out in the temperature range of 300 - 670 K between the pressure of 5.5 - 11 Torr, using a discharge-flow apparatus. n-Butanethiol, n-butane, and 1-butene are the main products at room temperature. The results are explained by the ring opening reaction initiated by the H atom attack on sulfur atom, followed by the C-S bond dissociation.

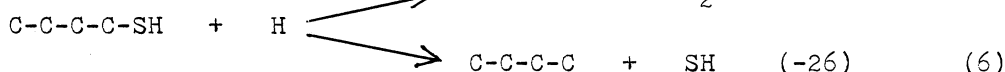
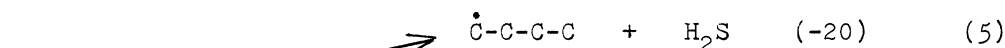
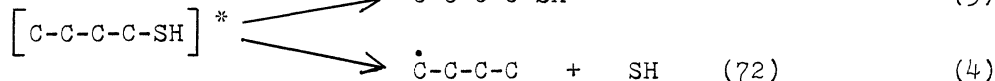
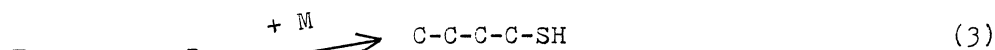
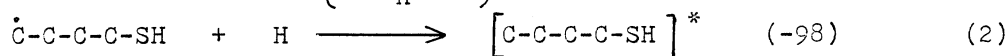
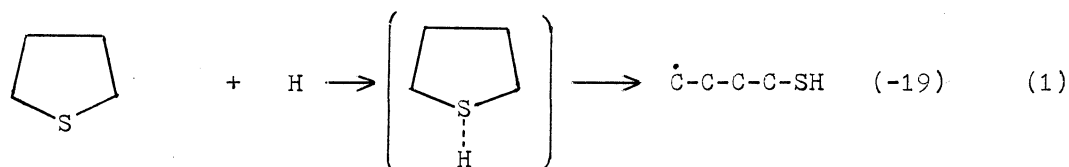
The reactivity of sulfur compounds toward H atoms poses interesting problems concerning the relationship between the molecular structure and the site of H atom approach. We have recently shown<sup>1)</sup> that the reaction of thiophene with H atoms was marked by the absence of sulfur-containing products other than H<sub>2</sub>S, and that this was explained by the initial H atom attack on the carbon atoms adjacent to the sulfur atom, followed by ring cleavage and sulfur atom elimination, forming butadiene and sulfur atom as the primary products. However, the possibility of the initial H atom attack on the sulfur atom was not excluded. We wish to report the results of thiolane-H atom system investigated to establish the mechanism of the reactions of sulfur compounds with H atoms in gas phase.

The reaction was carried out using the apparatus and procedure similar to those described in our previous work.<sup>1)</sup> Basically, the apparatus consisted of discharge-flow reactor, thiolane vaporizer, U-tubes for trapping products, flow control lines, and evacuation unit. The reaction products were analyzed by gas chromatography. Only qualitative description will be given for methane and H<sub>2</sub>S since their quantitative analyses were uncertain. The experimental conditions were: temperature range of 300 - 670 K and pressure of 5.5 - 11 Torr.

The change of the product selectivity with the conversion is illustrated in Figure 1 for the runs at 295 K and 5.5 Torr. The lowest conversion of thiolane in this study was about 70%. Even for such relatively high conversion, approximately 80% of the products consisted of n-butanethiol. The rest was shared by n-butane(10%), 1-butene(5%), C<sub>3</sub>(2%), C<sub>2</sub>(2%), and other minor products including cis- and trans-2-butene, and some C<sub>8</sub> hydrocarbons. The selectivity of n-butanethiol decreases as the conversion increases, while this decrease is almost exactly compensated by the increase of n-butane.

A reaction scheme consistent with the above observation is expressed by the reactions (1) to (6). Figures in parentheses are estimated values of the heat of reaction  $\Delta H$  in kcal/mol,<sup>2)</sup> and the asterisks indicate vibrational excitation. The values of  $\Delta H$  for the reactions (2) and (4) are based on the heat of formation

of n-butanethiol.



The ring opening reaction initiated by the H atom attack on sulfur followed by the concerted C-S bond dissociation to form 4-mercapto-1-butyl radical  $\dot{\text{C}}_4\text{H}_8\text{SH}$  (1) is in accord with the experimental results. The subsequent H atom attack produces the energized n-butanethiol (2), which in turn undergoes either collisional stabilization to n-butanethiol (3), or decomposition to 1-butyl radical and SH radical (4). 1-Butyl radicals disproportionate to n-butane and 1-butene, or associate to form n-octane. It is seen in Figure 1 that n-butanethiol, n-butane, and 1-butene

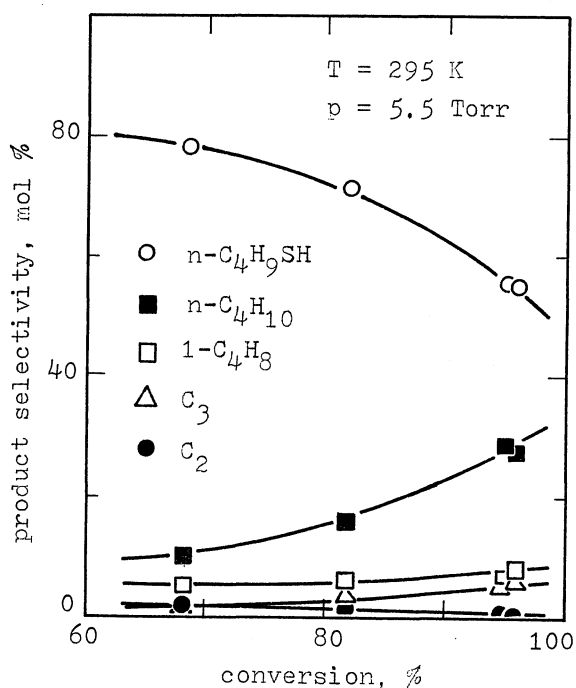


Fig. 1. The change of the product selectivity with conversion.

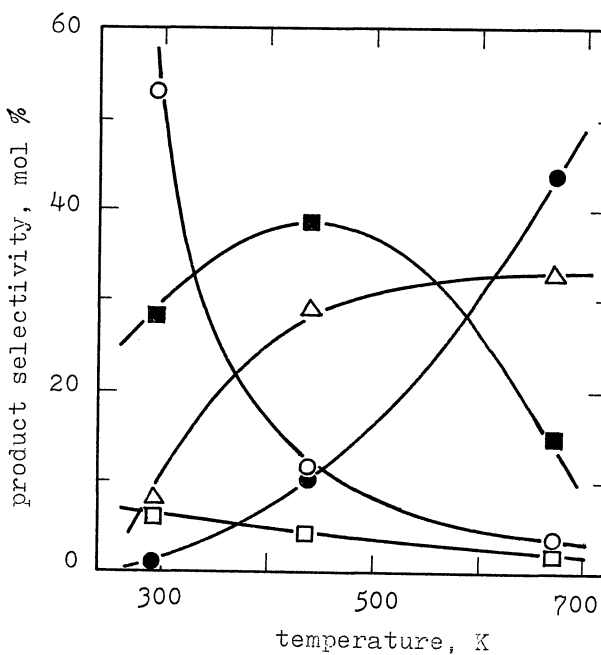
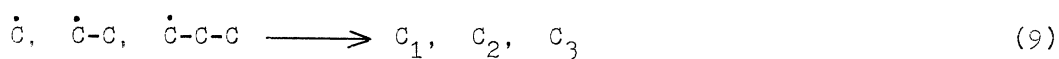
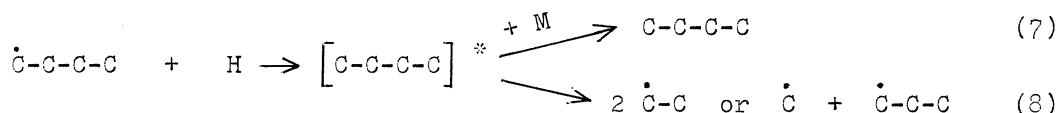


Fig. 2. The effect of temperature on the product selectivity. The symbols are the same with Fig. 1.

account for more than 90% of the sum of the product selectivity. Thus, the reactions (1) to (4) are consistent with the experimental results for lower conversion range, say less than 60%. Under this particular condition, more than 80% of the energized thiol is considered to be stabilized to n-butanethiol. In the reaction scheme, the reaction of  $H_2$  with  $\dot{C}_4H_9SH$  radical was not included since its contribution was considered minor.<sup>3)</sup>

When the relative concentration of H atoms is large, the products of the primary reaction, n-butanethiol and 1-butyl radical, may further react with H atoms. The reactions (5) and (6) are energetically feasible for butanethiol. In order to examine the significance of these reactions, a few experiments on n-butanethiol were carried out at about 350 K and 5.5 Torr. In one run of 50% conversion, the relative yield of the main products was: n-butane 66%, 1-butene 14%,  $C_3$  14%, and  $C_2$  0.6%. This can be compared with the reaction of thiolane at high conversions. Thus for 95% conversion of thiolane (Figure 1), the relative yield of the products excluding n-butanethiol is: n-butane 67%, 1-butene 16%,  $C_3$  10%, and  $C_2$  0.5%. The striking similarity between these product distributions indicates that n-butanethiol formed in the reaction (3) reacts with H atoms, giving rise to n-butane as the main product through the reactions (5) and (6). This explains the decrease in n-butanethiol which is nearly counterbalanced by n-butane for higher conversion range, although the relative importance between the reaction (5) and (6) can not be determined at this stage. Slight difference in the product distribution may be regarded as arising from the temperature difference between the thiolane and the n-butane-thiol cases.

Since this is a typical chemical activation system, the relative importance between the reactions (3) and (4) should be affected by both temperature and pressure.<sup>4,5)</sup> The effect of temperature upon the selectivity is shown in Figure 2 for high conversion (> 95%) and at 5.5 Torr. First, the drastic decrease in the thiol selectivity with temperature is seemingly due to the relative decrease in the rate of stabilization (3) with respect to that of decomposition (4). Second, the change in the hydrocarbon selectivity with temperature is caused mainly by the reactions of 1-butyl radical formed in (4) with H atoms. These reactions may be summarized as follows.



The reaction of n-butyl radical with  $H_2$  is not included.<sup>3)</sup> When the temperature is not high, the major path of the decay of the energized n-butane is the collisional stabilization to n-butane (7). At sufficiently high temperature, the decomposition path (8) predominates, resulting in  $C_1$  through  $C_3$  as final cracked products by the reaction (9) which involves the radical disproportionation and H atom addition reactions. Thus, the observed curves in the selectivity of n-butane and of  $C_2$  and  $C_3$  with temperature are interpreted by the reaction scheme involving chemically activated species.

The relative contribution of the reactions (3) and (4) should also be affected by the pressure. Such effects could not be examined in detail since the conversion was strongly affected by the pressure, which made it difficult to isolate the net effect due to the pressure. However, at temperature of 440 K for which the conversion changed from 97 to 88% as the pressure was increased from 5.5 to 11 Torr, the changes of the product selectivity were: n-butanethiol 13 to 40%, n-butane 40 to 20%, 1-butene 4 to 15%,  $C_3$  30 to 16%, and  $C_2$  10 to 3%. These results are basically in accord with the predicted effects of the pressure upon the energized species  $n-C_4H_9SH^*$  and  $n-C_4H_{10}^*$ . Thus, associated with the pressure increase are (a) the relative increase in the stabilization rate as indicated by the increase in n-butanethiol and the decrease in n-butane, and (b) the decrease in the decomposition rates as evidenced by the increase in 1-butene and the decrease in  $C_2$  and  $C_3$ .

The results of the present study can be compared with a similar reaction of thiirane. Yokota et al.<sup>6)</sup> studied the reaction of thiirane with H atoms between 300 and 425 K under the hydrogen pressure of about 500 Torr, using Hg photo-sensitization. Ethylene and hydrogen sulfide were the only retrievable products, although the deposit of elemental sulfur was observed on the reactor wall. Ethanethiol was found to be completely absent. The sole primary reaction was reported to be sulfur atom abstraction,  $H + C_2H_4SH \rightarrow C_2H_4 + SH$ . This is a unique reaction in that a divalent atom is abstracted by a monovalent radical. The absence of ethanethiol in the products suggests that there is little possibility of the primary reaction similar to the reaction (1) in the thiolane-H system. The energized radical  $\dot{C}H_2CH_2SH^*$  would be effectively stabilized under the pressure of 500 Torr, eventually leading to ethanethiol.<sup>7)</sup>

On the other hand, the reaction of thiolane with H atoms is characterized by the formation of n-butanethiol, which indicates that the H atom addition to sulfur atom followed by the ring opening is the primary reaction. Further studies on thietane and other sulfides are due in order to examine the relationship between the reactivity of the sulfide rings toward H atoms and the molecular structure.

#### References and Notes

- 1) O. Horie, N. H. Hanh, and A. Amano, Chem. Lett., 1975, 1015.
- 2) S. W. Benson, "Thermochemical Kinetics", John Wiley, New York, 1968.
- 3) The effect was estimated as at most 8% of the reaction (2) at 700 K, with the activation energy of the H atom abstraction reaction of 10 kcal/mol and  $[H] / [H_2]$  of 0.01.
- 4) For chemical activation, see, for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, London, 1972, Chapt. 8.
- 5) A. Amano, O. Horie, and N. H. Hanh, Intern. J. Chem. Kinet., 8, No. 3, in press.
- 6) T. Yokota, M. G. Ahmed, I. Safarik, O. P. Strausz, and H. E. Gunning, J. Phys. Chem., 79, 1758(1975).
- 7) The conditions of 300 K and 500 Torr are generally considered sufficiently favorable to the collisional stabilization of simple energized radical or molecule composed of five or six atoms. See ref. 4 for a detailed account.

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