(overlapping signals, 9 H), 3.04 (m, 1 H), 11 δ 1.16 (d, 7 Hz, 3 H), 1.50–1.70 (overlapping signals, 9 H), 2.60 (m, 1 H); MS *m/e* (rel intensities) 144, 146 (13, 5), 109 (18), 108 (30), 93 (100).

1-(1-Chloroethyl)-1,2,3,4,5-pentamethylcyclopenta-2,4-diene (12): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.07 (d, 6.5 Hz, 3 H), 1.13 (s, 3 H), 1.60–1.90 (overlapping signals, 15 H), 4.15 (q, 6.5 Hz, 1 H); MS *m/e* (rel intensities) 198, 200 (9, 3), 163 (39), 162 (30), 147 (100), 135 (13); IR (neat) 1670, 1660 cm^{-1}. These data were identical with those of an authentic sample, prepared by a known procedure.[12]

Acknowledgment. We are grateful for support of this work by BASF Aktiengesellschaft, Chemische Werke Hüls, Deutsche Forschungsgemeninschaft and Fonds der Chemischen Industrie.

Registry No. 1, 71031-67-9; 2, 71049-88-2; 3, 71049-89-3; 4, 71049-90-6; 5, 71031-68-0; (±)-(R^*,R^*)-6, 70359-35-2; 7, 71031-69-1; 8a, 71031-70-4; 8b, 71031-71-5; 8c, 71031-72-6; 8d, 71031-73-7; 9, 71031-74-8; 10, 71031-75-9; 11, 71031-76-0; 12, 19835-61-1; 26, 87-85-4; 27, 700-12-9; 2-butyne, 503-17-3; 2,2-dichlorobutane, 4279-22-5; 2-chloro-1-butene, 2211-70-3; (*Z*)-2-chloro-2-butene, 2211-69-0; (*E*)-2-chloro-2-butene, 2211-68-9; hydrogen chloride, 7647-01-0.

Gas-Phase Reaction of Benzothiophene with Hydrogen Atoms

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Reaction of benzothiophene with hydrogen atoms was studied at a pressure of 8 torr and at temperatures ranging from 423 to 853 K by using a conventional discharge flow reactor. 1-Thiaindan, dihydro-1-thiaindans, and dihydrobenzothiophenes were the main products at lower temperatures. But at higher temperatures, phenyl vinyl sulfide became the outstanding product. The sharply contrasted reactivity of benzothiophene as compared with that of thiophene was accounted for by a unique 3-position attack by a hydrogen atom and in terms of chemically activated intermediates.

The gas-phase reactions of the thiirane–hydrogen system[1] and 3-thiolene–hydrogen system[2] at room temperature have been shown to form ethylene and butadiene, respectively. A unique one-step abstraction of divalent sulfur by a H atom has been proposed as a plausible mechanism in these instances where the reaction path is highly stabilized by π conjugation. In the thiolane–hydrogen system, on the contrary, the sulfur elimination has been shown to take place through chemically activated butanethiol.[3]

The highly specific desulfurization of thiophene in its reaction with H atoms has been suggested to proceed through the reaction path distinctly different from those of the two typical cases mentioned above. Butadiene, the exclusive product of the system, could be formed via energized 3-thiolene[2] or alternatively via the 1,3-butadienylthio radical.[4]

The present study deals with the gas-phase reaction of the benzothiophene–hydrogen system as an extention of the series and intends specifically to clarify the role of chemically activated intermediates in the course of the sulfur elimination and to relate the possible mechanism with that of the thiophene–hydrogen system.

Experimental Section

The apparatus, full details of which have been described elsewhere,[5] consists of a quartz discharge flow reactor of 350-mm length and 27-mm diameter. The reaction was carried out under a total pressure of 8 torr and at temperatures ranging from 423 to 853 K. The temperature was measured by a chromel–alumel thermocouple placed along the central axis of the reactor and was maintained within ±2 K of the recorded value through the reaction zone.

Table I. Reaction of Benzothiophene

		flow rate, μmol/s				
T, K	*P*, torr	benzothiophene × 10^2	H_2	N_2	reacn time, s	convrsn, %
423	8.0	1.58	37.1	52.1	0.40	7.3
465	8.3	0.61	31.9	51.6	0.39	13.7
568	8.0	1.96	36.6	52.1	0.29	12.3
673	8.3	1.65	36.6	51.6	0.26	12.0
733	8.2	1.06	36.1	51.6	0.23	9.8
785	8.0	0.80	37.3	51.6	0.21	15.9
853	8.0	0.16	37.3	51.6	0.19	9.5

Substrate vapor was introduced along with flowing nitrogen into the reactor from a reservoir immersed in a bath thermostated at temperatures from 353 to 363 K. Products were first collected in an ampule chilled by liquid nitrogen, then dissolved in ether, and finally analyzed by a gas chromatograph equipped with a flame ionization detector. GC peak areas were corrected for detector response. Gaseous products isolated by bulb-to-bulb fractionations were directly introduced into the GC column. A combined GC/MS technique was used for the identification of sulfur compounds.

Commercial reagent grade benzothiophene, having more than 98% purity as analyzed by GC, was used without further purification. Phenyl vinyl sulfide,[6] 1-thiaindan,[7] and *o*-ethyl-

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[1] T. Yokota, M. G. Ahmed, I. Safarik, and O. Strausz, *J. Phys. Chem.*, **79**, 1758 (1975).

[2] O. Horie, J. Nishino, and A. Amano, *J. Org. Chem.*, **43**, 2800 (1978).

[3] O. Horie, K. Onuki, and A. Amano, *J. Phys. Chem.*, 81, 1706 (1977).

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[5] O. Horie and N. H. Hanh, *J. Phys. Chem.*, **80**, 1675 (1976).

[6] F. Montanari, *Boll. Sci. Fac. Chim. Ind. Bologna*, 14, 55 (1956); *Chem. Abstr.*, 57236 (1957).

[7] S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Inst. Pet., Abstr.*, **40**, 76 (1954).

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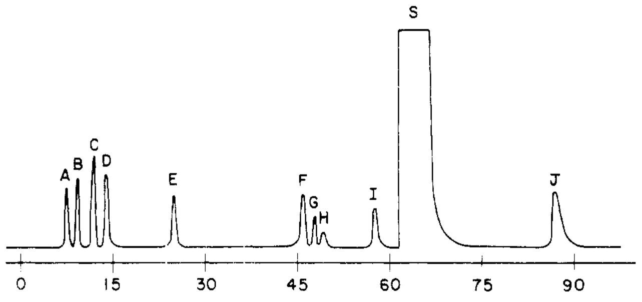


Figure 1. GC elution diagram of products (45-m Apiezon L capillary column, 383 K, carrier gas N_2): (A) benzene, (B) toluene, (C) ethylbenzene, (D) styrene, (E) phenyl vinyl sulfide, (F–H) dihydro-1-thiaindans, (I) dihydrobenzothiophene, (J) 1-thiaindan, (S) benzothiophene.

benzenethiol,[8] used for identification purposes, were prepared by the methods described in the literature cited.

Results

No products were detected whatsoever when benzothiophene (**1**) and molecular hydrogen were introduced into the reactor at 950 K without hydrogen discharge. The presence of H atoms is, therefore, indispensable for the reaction of **1** to take place.

Listed in Table I are conversions of **1** observed under varying reaction conditions. The conversions were calculated on the basis of the volatile products having six or more carbon atoms. Illustrated in Figure 1 is a typical GC elution diagram of the products as separated on a 45-m Apiezon L capillary column. Peaks from A to J are designated in their order of retention time.

Immediately apparent is the formation of four desulfurized products, i.e., benzene, toluene, ethylbenzene, and styrene, in about equimolar amounts.

Peak E can be attributed to phenyl vinyl sulfide (**2**) on the basis of GC retention time. The special feature of **2** was its complete absence from the products obtained at lower reaction temperatures.

That peaks F–H stand for three isomers of dihydro-1-thiaindan (**3**) can be deduced from the intense signal at *m/e* 138 (relative abundance 930) corresponding to molecular ion of **3**. Separate characterization of these peaks by NMR spectroscopy was unsuccessful. *o*-Ethylbenzenethiol (**4**), another conceivable product from **1**, should also give the parent ion signal at the same *m/e* value. But, the absence of **4** was confirmed by both GC retention time and mass fragmentation pattern analyses. A silicon oil packed column was used for the GC analysis of the thiols.

Peak I is considered to be due to dihydrobenzothiophene (**5**) in view of the intense signal at *m/e* 136 (relative abundance 942) corresponding to its molecular ion. The signals at *m/e* 135 (relative abundance 692) and 134 (relative abundance 1000) seem to arise from the subsequent fragmentations of the molecular ion, the latter of which is due to **1**. It appears that only one of the three isomers of **5** was separated as peak I, the other two being overlapped with **1** which is present in an overwhelming amount. Although not important, this may cause a slight underestimation in the rate of H-atom attack to the benzene ring of **1** reported here. Peak J can be attributed to 1-thiaindan (**6**) on the basis of GC retention time and mass spectral pattern, both of which are in agreement with those of the reference compound.

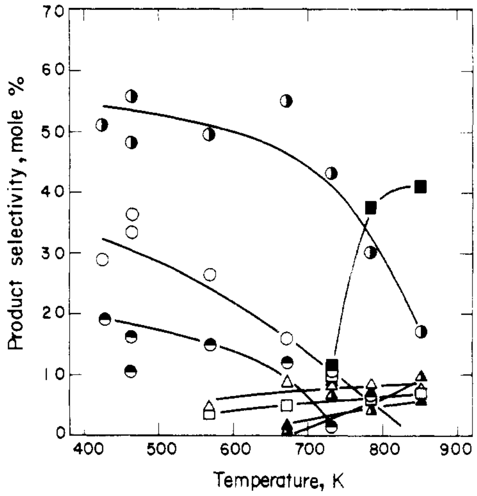


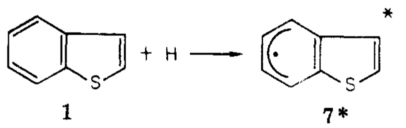
Figure 2. Product selectivity vs. temperature: (◑) 1-thiaindan, (○) dihydro-1-thiaindans, (⊖) dihydrobenzothiophene, (□) styrene, (△) ethylbenzene, (▲) toluene, (◭) benzene, (■) phenyl vinyl sulfide.

Aside from those mentioned above, C_2 and C_3 hydrocarbons (<10 mol % of the total products) were also formed. They will be ignored in the subsequent discussion where attention is mainly devoted to the formation of larger molecular species.

Illustrated in Figure 2 is the effect of temperature upon the distribution of the volatile products. The contamination of the vessel wall by nonvolatile materials was not detected after more than a dozen repeated runs. The products can be divided into two classes. One group consists of those expected from the initial H-atom attack to the thiophene ring of **1**. This includes **2**, **3**, and **6** and also benzene, toluene, ethylbenzene, and styrene. On the other hand, the initial attack to the benzene ring of **1** gives rise to the formation of **5**. The results illustrated here clearly indicate that the former is by far the more important reaction route. It should also be noted that the hydrogenation products, i.e., **3**, **5**, and **6**, were the main products at 423 K but were overtaken by **2** at higher temperatures.

Discussion

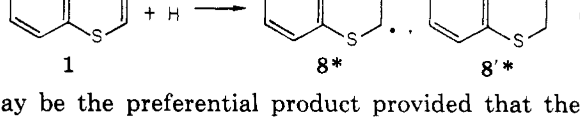
Hydrogen atom initially adds to the benzene ring of **1** (reaction 1). An asterisk denotes a vibrationally energized



(1)

species. The chemically activated radical **7*** is stabilized, eventually giving rise to the formation of three isomers of **5**, at lower temperatures, or is lost by pyrolytic fragmentations at sufficiently high temperatures. This view, taken after hitherto known reactions of the structurally similar cyclohexadienyl radical, is in accordance with the trend in Figure 2.

However, a still more important initial act of the H atom is the addition to the thiophene ring of **1** leading to the formation of either the 1-thiaindan-2-yl radical (**8***) or the 1-thiaindan-3-yl radical (**8′***) (reaction 2). Of these, **8′***



(2)

may be the preferential product provided that the 2-

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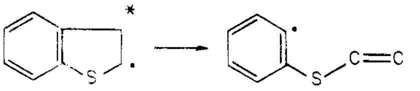
[8] C. Hansch and W. A. Blondon, *J. Am. Chem. Soc.*, **70**, 1561 (1948).

position of 1 is more susceptible for H-atom attack as in the case of thiophene.[2,4,9] The simple analogy is, however, open to question. Thus, it was pointed out earlier that the reactive site of 1 for electrophilic substitution was its 3-position rather than its 2-position as was the rule for thiophene.[10] The observed difference between 1 and thiophene was further accounted for by the stabilization energy of the transition states involved.[11] But the same MO calculation, when applied to radical attack, resulted in a controversy due to the complexity caused by possible energy crossing in the course of activated complex formation.[11] It is more adequate here to assume that a H atom attacks the 3-position of 1, simply because of the absence of *o*-vinylbenzenethiol and because of the presence of phenyl vinyl sulfide in the products. It should be noted that both phenyl vinyl sulfide and *o*-vinylbenzenethiol are not quite stable at the temperature studied. However, preliminary tests of these compounds for a purely thermal reaction revealed that at 800 K they remained unreacted for a residence time of 0.7 s. The present case offers the first example of the neutral-atom addition in which 1 and thiophene show distinctly different behavior.

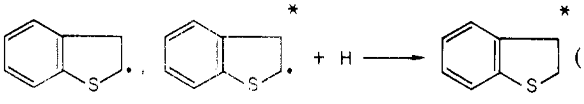
The chemically activated radical **8*** thus produced undergoes either stabilization or decomposition depending on the conditions used (reactions 3 and 4). It should not be unrealistic to suppose that a larger number of internal degrees of freedom favors **8*** to be stabilized to form **8**. This is one aspect in which the reactivity of 1 differs from that of thiophene. Although an RRKM calculation cannot be achieved due to the uncertainty in potential energies and vibrational frequencies of the species involved, it has been pointed out that an increase in the internal degrees of freedom from 32 to 140 would result in a decrease in the decomposition rate by a factor of 10^5.[12] At sufficiently high temperatures, however, the decomposition of **8*** leading to **9** emerges. The net result is, then, the formation of **2** at the cost of cyclic sulfides as is the trend illustrated in Figure 2.

8* 8 (3)



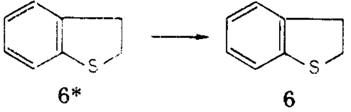
8* 9 (4)

Both **8** and **8***, then, react with a H atom.



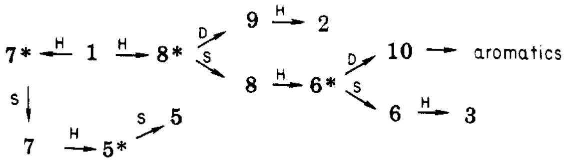
8 8* 6* (5)

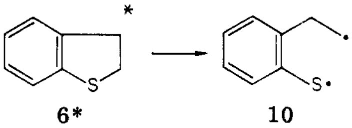
The chemically activated radical **6*** may have a fair chance to be stabilized at lower temperatures (reaction 6). Also expected from **6** is **3** by consecutive hydrogenations. **6**, as well as **3** to a lesser extent, was actually observed in low-temperature runs. At high temperatures, **6*** can easily decompose as in reaction 7. The formation of the biradical **10** through C–S bond cleavage may be compared with the decomposition of 2-oxolene known to proceed through a biradical intermediate.[13] It is interesting to note that, on the contrary, hydrogen was molecularly eliminated from 3-oxolene[14] and 3-thiolene[15] upon their pyrolyses.



6* 6 (6)

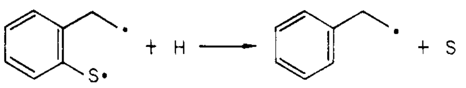
Scheme I





6* 10 (7)

To be consistent with the product selectivity observed, **10** must be desulfurized, presumably through reaction 8.



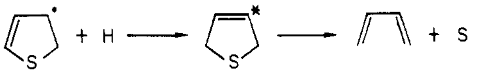
10 11 (8)

The radical **11** is the source of styrene and ethylbenzene. The latter, in turn, can account for the formation of benzene and toluene at high temperatures.

In summary, the reaction of **1** with H atoms forms **2**, **3**, **5**, **6**, and aromatic hydrocarbons through the network of Scheme I, where H, D, and S denote the H-atom addition, decomposition, and stabilization, respectively. Unfortunately, more complete elucidation of the scheme including energetics of the species involved and a D/S calculation is not possible at present.

In our previous communication,[2] two possible mechanisms leading to the formation of butadiene have been suggested for the thiophene–hydrogen system (reactions 9 and 10). Implications of the present study deserve some additional comments. If, contrary to the present view, **8′*** was the preferential intermediate, the mechanism via reaction 10 involving a double-bond shift would have to be ruled out in the reaction of **1** because of substantial loss in the resonance stabilization. It should be more likely, however, that **1** and thiophene undergo desulfurization through sharply contrasting pathways.

(9)



(10)

Acknowledgment. The authors are indebted to Professor Minoru Matsuda of The Institute of Non-Aqueous Solution, Tohoku University, for providing them with a sample of phenyl vinyl sulfide.

Registry No. **1**, 95-15-8; **2**, 1822-73-7; **3**, 71001-76-8; **5**, 71001-77-9; **6**, 4565-32-6; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; styrene, 100-42-5.

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