Specificity of Cyclic Sulfides in Gas-Phase Reactions with Hydrogen Atoms

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The reactivity of cyclic sulfides toward hydrogen atoms was studied by experimental work with 3-thiolene. The reaction was carried out at 295 K under the pressures of 670 Pa and 2.1 kPa in a conventional discharge-flow apparatus. Butadiene was found to be the primary product, which reacted further with hydrogen atoms to give butene isomers. No sulfur compounds except hydrogen sulfide were detected among the reaction products. The reaction is consistent with concerted sulfur atom abstraction by hydrogen atom. Comparison with the systems involving thiirane and thiolane indicates that concerted abstraction is characteristic of the system in which the reaction product of the sulfur abstraction is highly stabilized due to π conjugation.

The gas-phase reaction of thiirane with hydrogen atoms at room temperature has been known to give ethylene and hydrogen sulfide as the main products and is noted for the complete absence of ethanethiol even under the pressure of 66 kPa.[1] The reaction was explained in terms of a unique, concerted sulfur atom abstraction by the hydrogen atom, without the intermediacy of thio radicals which may lead to ethanethiol under high-pressure conditions.

On the other hand, 1-butanethiol was the predominant product in the reaction of thiolane with hydrogen atoms under a pressure of 660 Pa over the temperature range 300–580 K.[2,3] The initial hydrogen atom addition to the sulfur atom and the subsequent C–S bond cleavage to form 4-mercapto-1-butyl radical was considered responsible for the observed product distribution.

The marked difference in the reactivity of the two cyclic sulfides toward hydrogen atoms was suggested to be due to the difference in the stabilization of the reaction products.[3] The purpose of the present study is to examine the above presumption by investigating the reaction of 3-thiolene with hydrogen atoms in the gas phase and to relate the results to other cases of cyclic sulfides including the thiophene–hydrogen atom system.

Experimental Section

The reaction was carried out in a conventional discharge-flow reactor at 295 ± 2 K under pressures of 670 ± 20 Pa and 2.1 ± 0.03 kPa. The apparatus and procedure have been described in detail in our previous papers.[3,4] 3-Thiolene was prepared by the reduction of thiophene following the method of Birch and McAllan,[5] purified by gas chromatography (GC), and identified by NMR spectra.[6]

Two samples having different purities were used in the experimental work. One sample had a purity of about 95%, the impurity consisting mainly of 2-thiolene. The other sample, obtained by a further GC purification of the above sample, had a purity of 99% and contained no trace of 2-thiolene. The former sample was used in the majority of the experimental runs. Butadiene having more than 99% purity was also subjected to the reaction with hydrogen atoms under similar conditions. In all of the experiments, the change of the conversion was attained by shifting the position of the microwave discharge cavity for generating hydrogen atoms relative to the reaction zone.

The reaction products were analyzed by GC. In particular, the identification of butenethiols was inferred from the analysis of the reaction mixture of the Birch reduction of thiophene. After extracting thiolenes and unreacted thiophene by isopentane, the remaining alkaline solution was acidified and then extracted by isopentane. The GC analysis of the isopentane extract showed, besides thiophene and the thiolenes, the presence of four substances, presumably the isomers of butenethiols.[5] The relative retention times of the four GC peaks relative to that of thiophene were 0.87, 1.16, 1.32, and 1.36, using a silicone oil column at 80 °C.

Results and Discussion

The reaction products were found to be hydrogen sulfide and hydrocarbons consisting mainly of butadiene and butene isomers. In the high conversion-range runs (>50%) with the 95% purity sample, traces of four minor components were detected. They are considered most likely to be the isomers of butenethiols in view of the agreement of their retention times on GC with those observed for the four substances in the isopentane extract mentioned above. Since these products were not at all detected when the purer sample was used, it is clear that they were the products from 2-thiolene present as impurity. Therefore, they were not taken into consideration in the following discussion.

The change of the hydrocarbon selectivities with the conversion is illustrated in Figure 1. The products can be divided into three groups: butadiene, butene isomers, and the rest. Butadiene is apparently the primary product, from which result the hydrogenation products butene isomers. The third group products are considered derived from the reactions of the butene isomers with hydrogen atoms.

The distribution of the hydrocarbon products can be compared with that which arises from the reaction of butadiene with hydrogen atoms under similar conditions. The product distribution in the butadiene–H system was found to be more diverse than in the case with 3-thiolene–H. 3-Methyl-1-butene and *trans*- and *cis*-2-pentenes were among C_5–C_8 products which were not found in the 3-thiolene–H reaction products. However, the sum of the yield of these compounds never exceeded 15% of the sum of the yield of the reaction products. The comparison with the 3-thiolene–H system was therefore based on the products excluding the above C_5–C_8 products.

Since in the butadiene–H system the conversion corresponding to that for the 3-thiolene–H system cannot be defined, the following procedure was taken to effect the comparison. First, it is assumed that a total product mixture of a butadiene–H run represents the hydrocarbon product mixture of a 3-thiolene–H run. Secondly, the value of the conversion which gives the mole percent of butadiene equal to that found for the above mixture is read from the smoothed conversion–selectivity curve for butadiene in Figure 1. Finally, the selectivity of each of the hydrocarbons in the mixture is plotted at the particular conversion. The results are illustrated in Figure 2. The smoothed curves are the duplicates of those drawn in Figure 1.

It is clearly shown that the product distribution pattern of the butadiene–H reaction is identical with the hydrocarbon product pattern of the 3-thiolene–H reaction. This fact suggests that butadiene is formed exclusively in the initial reaction much faster than in the subsequent reactions, in which butadiene is consumed gradually by the remaining hydrogen atoms.

The reaction which leads to the undisturbed initial formation of butadiene is consistent with the concerted sulfur atom abstraction by the hydrogen atom via the transition state

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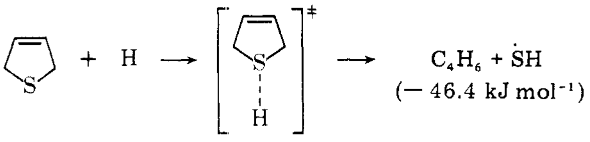
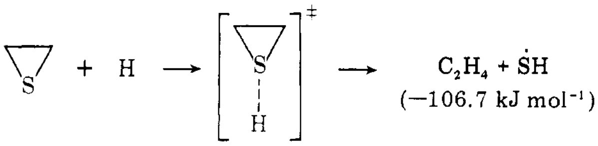
shown in the following scheme. This reaction scheme is very similar to that proposed for the thiirane–H system[1,7] in which



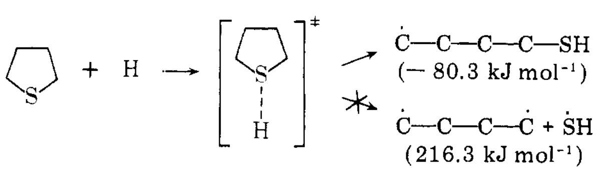
(1)



(2)

the divalent sulfur atom at the bridgehead position is abstracted by a monovalent radical. It is readily apparent in these examples that the hydrocarbon products are highly stabilized by π conjugation.

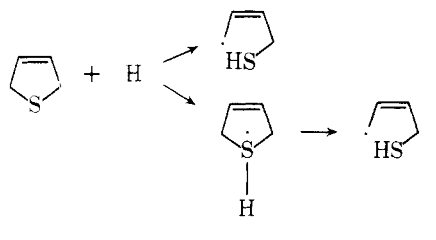
On the other hand, similar sulfur atom abstraction from thiolane is considered improbable, since the hypothetical product radical $\dot{C}$–C–C–$\dot{C}$ lacks the stability that is quite significant in 3-thiolene and thiirane cases. The formation of the mercaptobutyl radical by the cleavage of the C–S bond is instead the most probable path out of the transition state, as shown below.



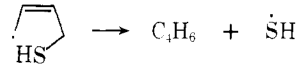
(3) (4)

Thus, concerted sulfur atom abstraction from the cyclic sulfides by a monovalent radical may be characteristic to the systems in which the product hydrocarbon is stabilized by π conjugation; otherwise C–S bond dissociation will be the primary step.

An alternative mechanism which seems also consistent with the experimental results may be considered. This involves the formation of the mercaptobutenyl radical (either in a direct displacement (5a) or in the fragmentation of the intermediate with the shell-expanded sulfur atom (5b)) followed by the elimination of the sulfhydryl radical (6).

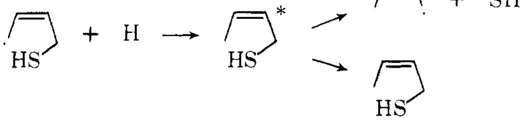


(5a) (5b)



(6)

The mercaptobutenyl radical may further react with hydrogen atom to form chemically activated butenethiols, which may either decompose to give butenyl and sulfhydryl radicals (7a, 7b) or collisionally stabilize to butenethiols (8a, 8b), depending on the reaction conditions.



(7a) (8a)

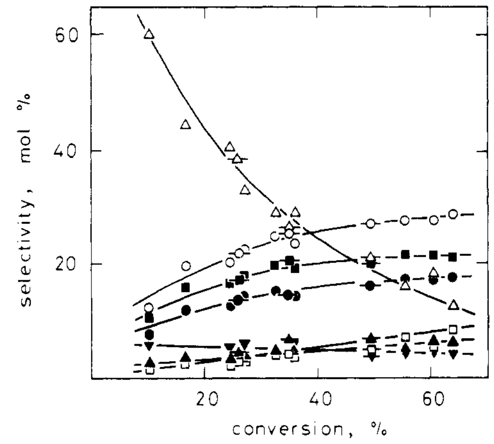


Figure 1. Conversion–selectivity relationship, 3-thiolene–H system, 295 K, 670 Pa: △, butadiene; ○, *trans*-2-butene; ○, *cis*-2-butene; ■, 1-butene; ▲, propylene; ▼, ethylene; □, *n*-butane. Symbols with the horizontal bars are the results of the 99% purity sample. The rest is based on the 95% purity sample.

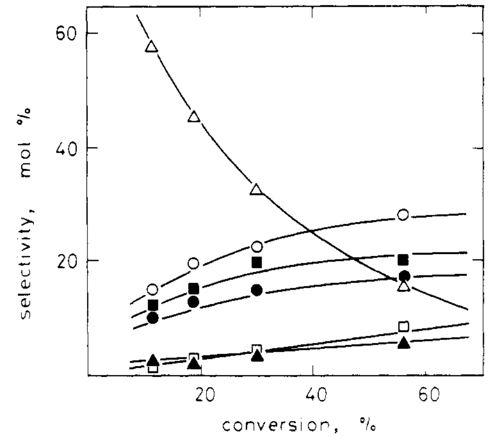
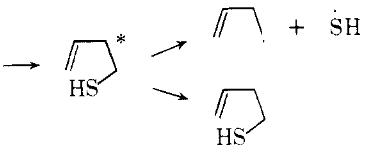


Figure 2. Conversion–selectivity relationship, butadiene–H system, 295 K, 670 Pa. For legends, see Figure 1. Results for ethylene are not shown due to its negligible formation.



(7b) (8b)

(The symbol * represents vibrational excitation.)

It has been shown, however, that under the present experimental conditions the isomers of butenethiol were not observed among the reaction products.[8] Therefore, it is considered that this two-step mechanism cannot adequately explain the experimental findings.

This aspect can further be substantiated by the results of the experiment carried out at 295 K under a pressure of 2.1 kPa where an enhanced stabilization should occur. In a typical run using the 99% purity sample with a conversion of 16%, the selectivity of the reaction products in mole percent was the following: butadiene 51%, *cis*-2-butene 11%, *trans*-2-butene 17%, 1-butene 16%, *n*-butane 1%, propylene 2%, and ethylene 3%. Formation of other products, in particular those assumed to be butenethiols, was hardly noticeable.

A somewhat similar observation was noted in the case of the reaction of thiirane with hydrogen atoms,[1] as mentioned earlier. It was stated that under a pressure of about 66 kPa, ethanethiol, the possible stabilization product, was shown to be demonstratively absent.

It is interesting to examine the relative yields of butene

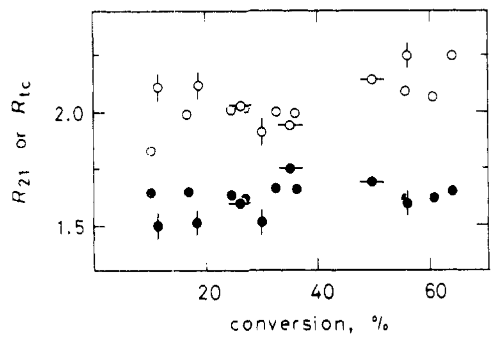
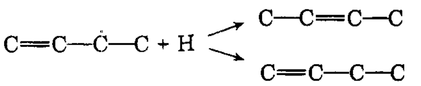


Figure 3. Conversion vs. R_{21} or R_{tc}, 295 K, 670 Pa: ○, R_{21}; ●, R_{tc}, 3-thiolene–H system. Symbols with the horizontal bars are the results of the 99% purity sample. Symbols with vertical bars are for butadiene–H system.

isomers in both 3-thiolene–H and butadiene–H systems. The reatios R_{21} = (2-butenes)/(1-butene) and R_{tc} = (*trans*-2-butene)/(*cis*-2-butene) are calculated and plotted against the conversion. The results are shown in Figure 3. The results of the 3-thiolene–H system are found to be the same as those for the butadiene–H system. Both R_{21} and R_{tc} are independent of the conversion. For the 3-thiolene case, the average values are calculated to be $R_{21} = 2.07 \pm 0.05$ (standard deviation) and $R_{tc} = 1.65 \pm 0.01$. These ratios are different from the equilibrium values $R_{21} = 41$ and $R_{tc} = 3.2$ at 300 K.

The comparable formation of isomers of 2-butene and 1-butene can be explained by the competitive hydrogen atom addition to the different carbon atoms of 1-buten-3-yl radical, formed by the predominantly terminal addition of the hydrogen atom to butadiene,[9] as shown below.

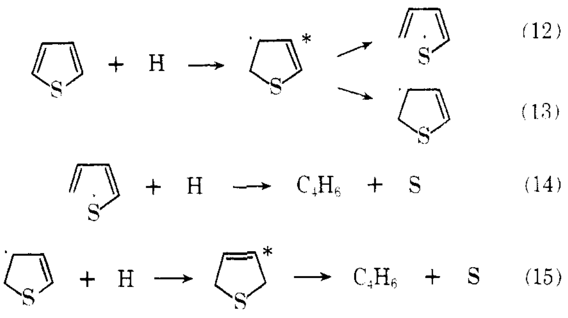
$$\mathrm{C{=}C{-}C{=}C + H \longrightarrow C{=}C{-}\dot{C}{-}C\ (C{\cdots}C{\cdots}C{-}C)} \quad (9)$$



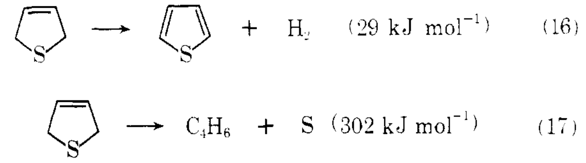
$$\mathrm{C{=}C{-}\dot{C}{-}C + H} \begin{cases} \longrightarrow \mathrm{C{-}C{=}C{-}C} & (10) \\ \longrightarrow \mathrm{C{=}C{-}C{-}C} & (11) \end{cases}$$

The restricted rotation about the central C–C bond of the radical due to the allylic stabilization[10] may account for the formation of the isomers of 2-butene in the moderately different ratio from the equilibrium.

The ratios R_{21} and R_{tc} for the thiophene–H system are found to be 1.51 ± 0.01 and 1.69 ± 0.20, respectively, for the conversion range of 2.5–18.4% at 300 K.[11] These values are very close to those observed for the 3-thiolene–H and butadiene–H systems, although 1-butene formation seems slightly more favored in the thiophene–H system. In this system, the formation of butadiene was explained by the decomposition of the unsaturated thio radical formed in step (12) upon the attack of a hydrogen atom, step (14). However, the results obtained for the 3-thiolene–H system, together with the fact that no sulfur compounds except hydrogen sulfide were found in the reaction products for the thiophene–H system, suggest an alternative process leading to the formation of butadiene. If the stabilized 2-thiolen-4-yl radical is formed in step (13), the chemically activated 3-thiolene is expected to be formed by the addition of a hydrogen atom to the thiolenyl radical. The activated 3-thiolene is then assumed to decompose completely to yield butadiene and the sulfur atom, step (15).



The last step (15) may be compared with the results of the pyrolysis of 3-thiolene in the gas phase.[12] Homogeneous elimination of hydrogen to form thiophene took place in the temperature range 610–690 K, step (16). It was noted, however, that hydrogen sulfide amounting to some 30% of the thiophene, together with a polymer material, was produced in addition to the equimolar mixture of hydrogen and thiophene. It was noted also that the hydrogen sulfide was possibly produced during the polymer formation. It can be speculated that the hydrogen sulfide was formed by the consequence of reaction 17. The endothermicity of reaction 17 of about 300 kJ mol^{-1} can be expected to be overcome once the reaction enters into some radical chain reactions in which the sulfur atom initiates the free radical chain leading to the accumulation of the polymer materials.



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Registry No.—3-Thiolene, 1708-32-3.

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