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REACTION OF THIOPHENE WITH ATOMIC HYDROGEN IN GAS PHASE

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Thiophene was subjected to the reaction with hydrogen atom under reduced pressure in the temperature range of 300 - 700°K, using a discharge-flow reactor. Butadiene, butenes, n-butane, propylene, and C_2 hydrocarbons are the main products, and no formation of sulfur-containing products other than hydrogen sulfide is observed.

Gas-phase reactions of aromatic hydrocarbons with hydrogen atom at room temperature are known to give H-addition products with minor ring-opening reactions.$^{1)}$ When thiophene was subjected to the reaction with atomic hydrogen in gas phase under reduced pressure, ring-opening associated with elimination of sulfur atom was found to be the predominant reaction, being markedly different from the case of the aromatic hydrocarbon - H systems.

Experimental work was carried out using a conventional discharge-flow reactor made of quartz tubing of about 300 mm in length and 27 mm i. d., in the temperature range of 300 - 700°K, under the pressure of 5.5 torr. Thiophene with more than 99.9 % purity was vaporized at the temperature of -35 ~ -50°C, diluted with a large flow (~ 3 ml-NTP/sec) of nitrogen, and introduced into the reactor. Atomic hydrogen was generated by microwave discharge of hydrogen (~ 0.35 ml-NTP/sec) at 2540 MHz. The relative concentration of hydrogen atom as measured by ethylene titration$^{2)}$ was approximately of the order of 0.1 % of H_2. The mole fraction of thiophene was in the range of $10^{-3} \sim 10^{-4}$. A typical run lasted for about 10 minutes during which the reaction products were collected in a liquid N_2 cooled trap, which was then subjected to GC analysis. No analysis of methane was attempted since it was not trapped by the above procedure. Hydrogen sulfide was analyzed qualitatively by reaction with Hg^{++}.

Experimental results are shown in Figures 1 and 2. The main products at room temperature are C_2 (ethane and ethylene), propylene, n-butane, cis- and trans-2-butene, 1-butene, and butadiene. Methane was not analyzed, but is thought to be produced in the secondary reactions. Propane, isobutane, and isobutene were also formed but in the amount much less than the above products. In addition, small amount of C_5, C_7, and C_8 fractions were formed, the sum of which did not exceed 10 % of C_2 - C_4 fractions for almost all runs. No formation of sulfur-containing products such as dihydro- and tetrahydrothiophene, n-butanethiol, and n-butenethiols, or other possible sulfur compounds except hydrogen sulfide was observed. This is the most significant difference from the case of aromatic hydrocarbons, where cyclohexadienes, cyclohexene, and cyclohexane from benzene, and their methyl derivatives from toluene[1,3]) were the dominant products under similar experimental conditions.

The relative yields of C_2 - C_4 products are plotted against temperature in Figure 1 for runs with conversions of 2.5 - 7.0 %. The effect of temperature is noted in (i) the increase in the yield of butadiene and propylene, and (ii) the decrease in the yield of butenes, n-butane, and C_2 with temperature. Increase in butadiene yield may be explained in terms of the decrease of the equilibrium constant for hydrogenation of butadiene to butene with temperature. Increase in propylene and decrease in n-butane may be explained by the secondary reactions of butene isomers with atomic hydrogen. Noting that the relative concentration of thiophene was about the same order of magnitude with that of hydrogen atom, it is quite likely that the secondary reactions compete with the primary H atom addition reaction. It has been shown that energized radicals formed by addition of H atom to butene isomers stabilize to butyl radicals, precursors of n-butane at low temperature, while decomposition to propylene and methyl radical becomes the preferred reaction path at elevated temperature.[4]) The decrease of C_2 hydrocarbons with temperature is not readily self-evident, in as much as ethane and ethylene were not separated.

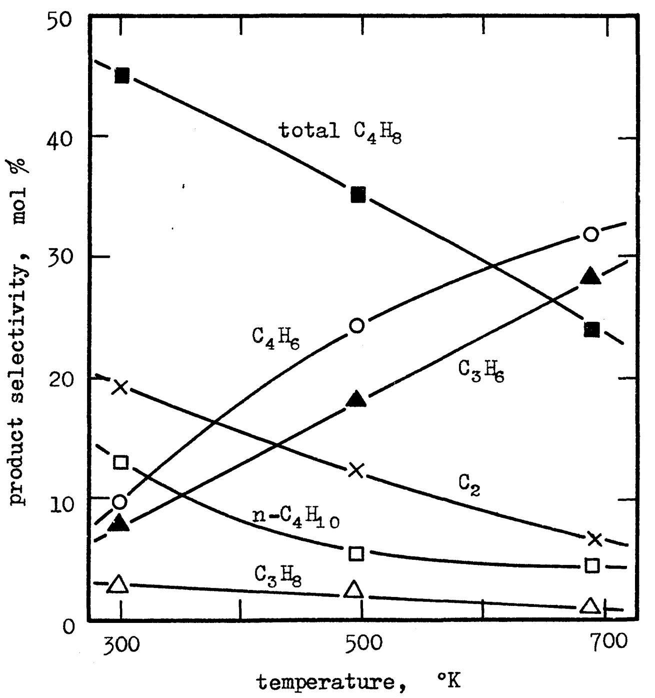


Figure 1. Product selectivity vs. temperature .

When the reaction was carried out at high conversion level, there was no essential change in the product pattern except the decrease in butadiene and increase in C_2 throughout the entire temperature range, although not shown here.

Since this reaction system can be regarded as a chemical activation system at least at room temperature, it was suggested that under the condition of higher pressure it might be possible to stabilize energized radical formed by the initial addition of H atom to thiophene, and eventually to isolate certain sulfur compounds as stable products. In order to examine this possibility, one run was conducted at room temperature under the pressure of 15.1 torr. With the conversion of about 23 %, the relative yield of each product is: C_2 19.3 %, C_3H_8 16.1 %, C_3H_6 9.5 %, n-C_4H_{10} 34.2 %, i-C_4H_{10} 1.1 %, C_4H_8(total) 19.1 %, and C_4H_6 0.6 %. Again, no sulfur compounds are found except H_2S. The only apparent difference between low pressure and high pressure runs is the increase of propane and n-butane, and decrease of butadiene in the latter case, where the condition should be favorable to the formation of hydrogenation products.

The ratio of 2-butene to 1-butene is plotted with respect to temperature along with the equilibrium ratio, in Figure 2. Also plotted in the figure are the results of butadiene - H experiment carried out under similar conditions. It is first noted that the experimental ratios are far away from the equilibrium ratio and practically temperature independent. Secondly the results of thiophene are almost indistinguishable from those of butadiene. The ratio of trans-2-butene to cis-2-butene for both reactants is found to vary from ~1.8 at 300°K to ~1.2 at 670°K. These values are smaller than the equilibrium ratio at corresponding temperature, ~3.2 and ~1.6 at 300 and 670°K, respectively, but not as much as found in the case of 2-butene/1-butene. From these results, it is indicated that butadiene and hydrogen sulfide (not analyzed quantitatively) are the primary stable products, the former of which then undergoes further reaction with H atom.

Initial addition of H atom to thiophene will now be considered. Results of ESR spectra of radicals formed by addition of H atom to thiophene and furan at liquid N_2 temperature$^{5)}$ indicate

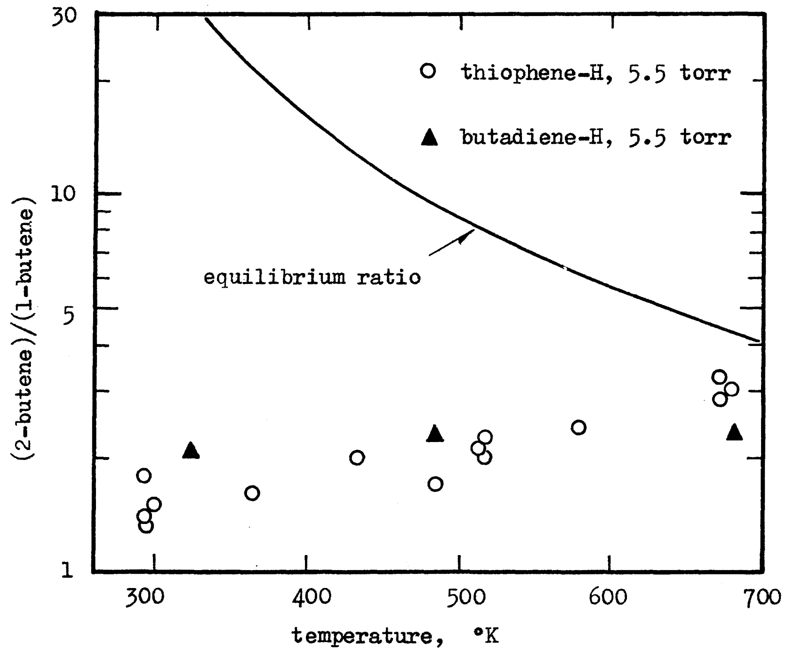
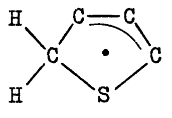
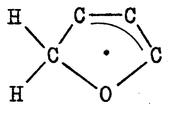


Figure 2. Ratio of 2-butene to 1-butene vs. temperature.

that H atom addition occurs at the 2-position of the ring, resulting in the formation of radicals of the form shown as (I) and (II) for thiophene and furan, respectively. Recent pulse-radiolysis studies in aqueous solutions indicate that OH or H addition to 2-position of pyrrole,6) and furan7) occurs selectively. In view of this high selectivity, the initial H atom addition to thiophene in gas phase can be considered at the carbon atoms adjacent to the sulfur atom. The energized radical so generated is considered then to undergo ring cleavage.

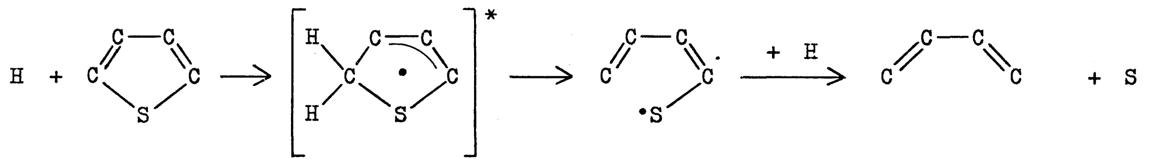


(I)



(II)

This step may be justified by noting that similar cleavage is found to occur with pyrrole - OH reaction in acidic media8) and with furan - OH reaction in basic solution.7) Upon further attack of H atoms, the above radical will decompose to give butadiene and atomic sulfur, as shown below.



This scheme excludes possibility of formation of sulfur compounds other than H_2S by a highly exothermic reaction with hydrogen, in accord with the present results.

In order to check the possibility of formation of the radical (I), and hence of finding sulfur compounds in the products, a few runs were made in which stream of atomic hydrogen was passed through a surface coated with a film of thiophene at liquid N_2 temperature and analyzing after warming up to room temperature. Although the results are not yet conclusive, tetrahydrothiophene and n-butanethiol as searched by GC analysis were not found among the reaction products. Extensive studies on this and other heterocyclic compounds - H atom systems are under way.

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