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NOTES

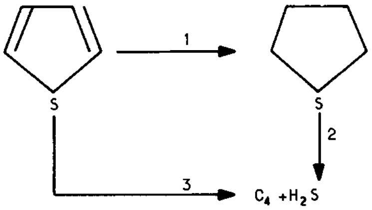
Hydrogenolysis and Hydrogenation of Thiophenic Compounds on a Co-Mo/Al_2O_3 Catalyst

The catalytic desulfurization of petroleum fractions is mainly a reaction of hydrogenolysis of thiophenic compounds. The subject has been extensively treated in several comprehensive reviews (*1*). After the publications of Amberg and co-workers (*2*), it is generally assumed that thiophene (T) desulfurization on MoS_2, Cr_2O_3, or Co–Mo/Al_2O_3 catalysts proceeds primarily by a C–S bond cleavage, according to the Lipsch and Schuit mechanism (*3*). However, the hypothesis of a preliminary hydrogenation of the thiophene ring has been suggested in some previous papers (*4*). Benzothiophene (BT) hydrodesulfurization has also been more recently investigated, with apparent conflicting data about the thiophenic ring hydrogenation reaction. Bartsch and Tanielian (*5*) as well as Furimsky and Amberg (*6*) found only hydrogenolysis resulting in ethylbenzene (EB), and in some cases styrene. On the contrary, Givens and Venuto (*7*) observed the formation of 2,3-dihydrobenzothiophene (DHBT) and the occurrence of a hydrogenation–dehydrogenation equilibrium between BT and DHBT. The dehydrogenation of DHBT to BT was confirmed by Furimsky and Amberg (*6*). Recognizing that there is a large pressure gap between these atmospheric pressure experiments and the industrial practice, de Beer and coworkers (*8*) and Daly (*9*) carried out their BT hydrodesulfurization studies under a medium H_2 pressure. Both groups found DHBT in the reaction products.

These discrepancies prompted us to investigate more closely the hydrogenation–hydrogenolysis reactions of T and BT under hydrogen partial pressures in the range found in commercial units.

The experiments were carried out in a conventional high-pressure stainless-steel downflow reactor. The sulfur compound diluted in *n*-heptane (1% sulfur by weight) was pumped from a buret, mixed with hydrogen and preheated before reaction. The catalyst used was commercial Ketjen 125 Co–Mo/Al_2O_3, diluted with inert crushed alumina, and presulfided by CS_2 diluted in *n*-heptane. The partial pressures of heptane and sulfur compounds were held constant at 13.1 and 0.4 bar, respectively, while that of hydrogen (p_H) was varied from 2.2 to 17.5 bars (1 bar = 10^5 Pa). The reaction products were identified by mass spectroscopy and analysed by glc.

The thiophene runs were carried out at 220°C. The reaction products were butane and butenes, H_2S and THT, the latter detected in all cases. The most general mechanism consistent with our observations is the following.



(1)

If we make the assumption, supported by previous experiments of our own, that in our experimental conditions each reaction is first order in sulfur compound, we can write

$$\frac{-dT}{dt} = (k_1 + k_3)T$$

and

$$\frac{dTHT}{dt} = k_1T - k_2THT,$$

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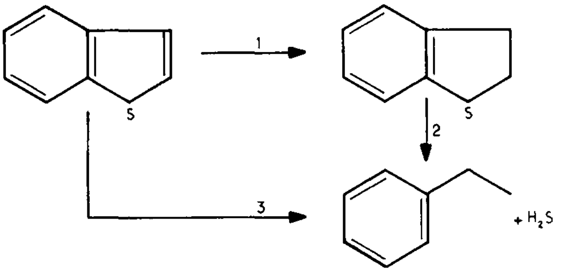
where k_1, k_2, and k_3 are apparent rate constants. With the initial conditions $T = T_0$ and THT = 0 these equations integrate to

$$T = T_0 e^{-(k_1+k_3)t},$$

$$THT = T_0 \frac{k_1}{k_2 - k_1 - k_3}\left[e^{-(k_1+k_3)t} - e^{-k_2 t}\right].$$

By the method of nonlinear regression, a set of k values was determined for each of the four hydrogen partial pressures studied. Yields of THT calculated with these k values are in fair agreement with the experimental data (Fig. 1). The linear relationship (Fig. 2) between k values and $p_H^{1/2}$ suggests, for each of the three reactions, an apparent kinetic order of 0.5 in hydrogen partial pressure.

The benzothiophene runs were carried out at 250°C yielding only ethylbenzene, H_2S, and DHBT. Under our experimental conditions other possible intermediates were certainly completely hydrogenated, as was checked for styrene. These results, quite similar to those obtained for T, lead us to suggest a mechanism of the same type:



(2)

The same assumptions as for the T case can be made, and values of apparent first-order rate constants were determined by a set of equations similar to those already detailed. Computed curves of DHBT

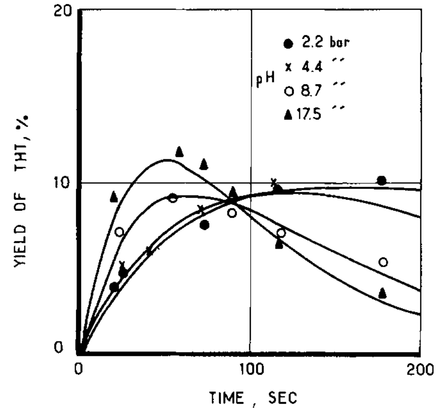


FIG. 1. Yield of THT versus time, for different H_2 partial pressures (p_H). Lines: calculated values. Single points: experimental values.

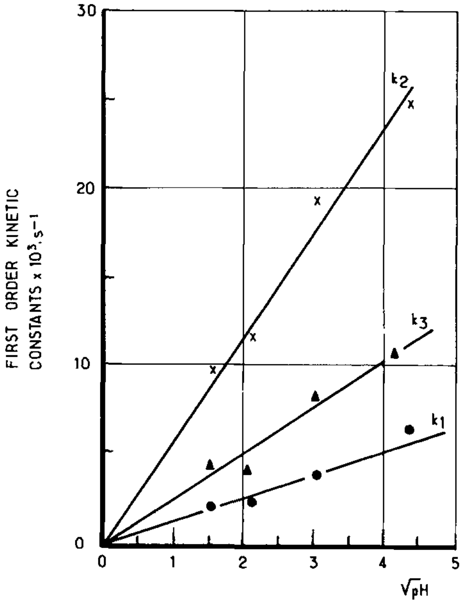


FIG. 2. Thiophene hydrogenolysis and hydrogenation first-order kinetic constants versus $p_H^{1/2}$. k_1, k_2 and k_3 refer to equation scheme (1).

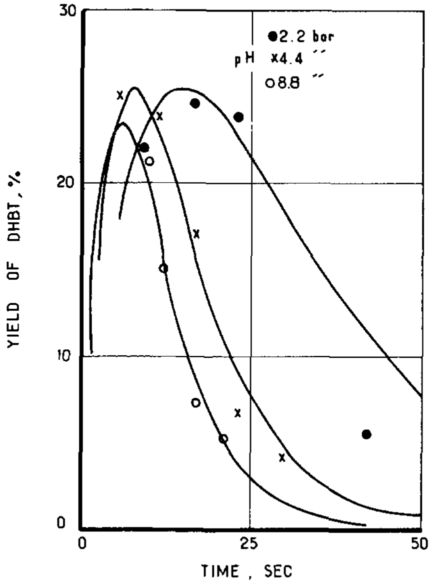


FIG. 3. Yield of DHBT versus time at different H_2 partial pressures. Lines: calculated values. Single points: experimental values.

yields, given in Fig. 3, are in good agreement with the experimental values. According to Fig. 4 we can also conclude that the three reactions have an apparent 0.5 order in hydrogen partial pressure.

Further experiments with several other alkyl- or dialkylthiophenes confirmed thiophene ring hydrogenation to be a general fact. The kinetic analysis of T and BT hydrogenolysis showing clearly two reaction pathways suggests to us the occurrence of two different catalytic sites, one for thiophene ring hydrogenation and the other for C–S bond scission.

This hypothesis is favored by several authors, for example, Hargreaves and Ross (*10*), and may be supported by some interesting experiments. In their work on hydrogen–deuterium exchange, Smith *et al.* (*11*) could detect, on Mo and Co–Mo catalysts, two types of sites: one was for α-exchange ascribed to thiophene desulfurization through sulfur adsorption, and the other for multiple exchange related to hydrogenation through possibly the flat adsorption of the molecule as a π-complex.

These two types of adsorption have also been suggested by Nicholson (*12*) after an infrared study of adsorbed thiophene on MoS_2.

In our case, and supporting this view, we can observe that benzothiophene, where the ring π-electron density and hence the π-complexing ability are higher than for thiophene, gives a larger ring saturation reaction (respectively, 77 and 35%).

We wish to answer the question of why THT and DHBT were not found in most low-pressure experiments with a suggestion. It should be noted that low-pressure experiments were generally run at high temperature, close to 400°C. On the contrary, the high-pressure studies were, like ours, carried out at lower temperatures (*8*, *9*). The hydrogenolysis reaction, resulting in C–S bond scission, has at both temperatures no practical thermodynamical limitation. However, thiophene ring hydrogenation is thermodynamically favored only at low temperature. For T and BT at 400°C, the equilibrium log k values are respectively −0.44 and −0.6. This might

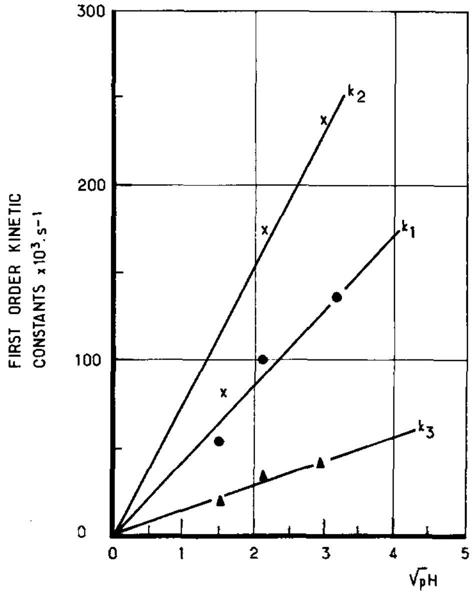


FIG. 4. Benzothiophene hydrogenolysis and hydrogenation first-order kinetic constants versus $p_H{}^{1/2}$. k_1, k_2, and k_3 refer to equation scheme (2).

explain the nonoccurrence of THT and DHBT at higher temperature, unless there is a large hydrogen excess (*7*), as pointed out by Furimsky and Amberg (*6*). This is also in good agreement with the equilibrium observed for BT by these authors (*6, 7*), as well as by Lee and Butt for T (*13*). However, the sensitivity of the catalysts to the activation procedure might be another reason which cannot be ruled out, but which would require further study.

For both T and BT hydrogenolysis and thiophene ring hydrogenation we find an apparent kinetic order of 0.5 in hydrogen partial pressure. Equations for such reactions have been reviewed in detail by Massoth (*14*). Referring to his discussion we can attempt an interpretation of the above observation by making the following assumptions: (1) dual-site mechanism, that is hydrogen adsorbed on one type of site and the thiophenic species on another one, (2) hydrogen adsorbed atomically, and (3) surface reaction of adsorbed species as the limiting step.

Since in our study the initial T and BT partial pressures $(p_s)_0$ have been held constant, the kinetic analysis can be made with a Langmuir–Hinshelwood adsorption term applied to hydrogen only, and results in the equation:

$$-\frac{dp_s}{dt} = \frac{kp_sp_H}{(1 + k_Hp_H)^{0.5}}.$$

For high p_H values, the second term tends toward $kp_sp_H{}^{0.5}/k_H$, that is the observed 0.5 order in hydrogen partial pressure.

It should be noted that the assumptions necessary for the kinetic analysis of our data are in perfect agreement with those of Lipsch and Schuit (*3*), who assumed the dual-site mechanism, and hydrogen atomically available as Mo–O–H and Mo–S–H.

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