JOURNAL OF CATALYSIS **80**, 491 (1983)

LETTERS TO THE EDITORS

Hydrogenation and Hydrogenolysis of Thiophenic Compounds: Correction and Comments

In a previous note (*1*) we reported experiments on the hydrogenolysis and hydrogenation of thiophene (T) and benzothiophene (BT). We used a quite wide range of hydrogen partial pressures, namely from 2.2 to 17.5 bar, and in both cases we found an apparent kinetic order for hydrogen which was close to 0.5.

Our interpretation was based on a Langmuir–Hinshelwood analysis [cf. Massoth (*2*)]. Unfortunately, the rate equation in our note (*1*) is incorrectly expressed and should be replaced by

$$-\frac{dp_s}{dt} = \frac{kp_sp_H}{1 + (K_Hp_H)^{0.5}}, \qquad (1)$$

where p_s and p_H are the partial pressures of T (or BT) and of hydrogen, respectively, k is the rate constant, and K_H is the equilibrium constant for dissociative adsorption of hydrogen. For high p_H values, the second term in the denominator becomes large compared to unity, and the right-hand side of Eq. (1) reduces to $(k/K_H^{0.5})p_sp_H^{0.5}$, thereby accounting for the observed 0.5 order in hydrogen.

Vrinat and de Mourgues (*3*) have recently reported data for this system and find them better fitted by

$$-\frac{dp_s}{dt} = \frac{kp_sp_H}{1 + K_Hp_H} \qquad (2)$$

and the same relationship has also been proposed by Broderick and Gates (*4*). Although Eqs. (1) and (2) are formally different, our experimental results, owing to their small number, can be fitted by both equations with about the same accuracy. Thus, within the scope of our experimentation, a 0.5 order in hydrogen partial pressure can be used for kinetic calculations, but more accurate work is needed to confirm a theoretically based kinetic equation.

ACKNOWLEDGMENT

We are indebted to Dr. M. Vrinat, Dr. C. Gachet, and Dr. L. de Mourgues for fruitful discussions and for pointing out to us the error in the rate equation.

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Received October 1, 1982

0021-9517/83 $3.00