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On the Mechanism of Thiophene Desulfurization

From preliminary experiments on the desulfurization of thiophene in the presence of deuterium, we have obtained results which appear consistent with an intriguing suggestion of Kolboe (*1*) regarding the mechanism of the reaction and which are subject to a simple kinetic explanation. Kolboe has noted a possibility, analogous to alcohol dehydration, that the initial step be an *intramolecular dehydrosulfurization* whereby the hydrogen contained in the hydrogen sulfide comes from positions *beta* to the sulfur of the parent molecule. The highly unsaturated surface residues—e.g., adsorbed diacetylene in the case of thiophene and adsorbed butadiene for tetrahydrothiophene—may then be hydrogenatively desorbed into the spectrum of observed products. On the other hand, previous proposals (*2*) have usually involved, at some point, the direct hydrogenolysis of the carbon–sulfur bond.

The use of deuterium, as a carrier for thiophene, to distinguish these mechanistic steps rests on the following expectations. If intramolecular dehydrosulfurization is involved, initial conversions will produce low values of the atom fraction of deuterium in the H_2S deutero-isomers, viz, $q_{H_2S} \equiv [(HDS) + 2(D_2S)]/\{2[(H_2S) + (HDS) + (D_2S)]\}$. On further conversion, this q-value will increase toward an equilibrium value, q_e, characteristic of complete statistical exchange (*3*). Oppositely, the direct hydrogenolysis of the carbon–sulfur bond to produce hydrogen sulfide would call for high initial q-values, which would decrease toward q_e with increasing conversion.

Our experiments were performed under the following conditions*:

Temperature, 288 to 343°C
Pressure, 400 psig
Deuterium/thiophene; 20/1 mole ratio
Deuterium/thiophenic hydrogen; 10/1 atom ratio ($q_e = 0.91$)
Contact time τ, 0.44 sec
Catalyst, 0.3 cc of cobaltia–molybdena–alumina (Harshaw 0601). The catalyst was presulfided with H_2S and thoroughly purged with deuterium at 427°C.

The product gas mixture was analyzed chromatographically on a 100 ft squalane column for thiophene conversion and, mass spectrometrically for the composition of the H_2S-like molecules. Following the fate of deuterium in the hydrocarbon moieties was deemed unwarranted, for these experiments, due to the complexities of the analyses.

The pertinent results of these experiments were:

Thiophene conversion, (mole %)	16	34	44	67	76
q_{H_2S} (atom fraction)	0.00	0.17	0.31	0.39	0.24

The absence of deuterium in the H_2S-like product at 16% conversion and the limited q-values over the observed conversion range lend substance to Kolboe's suggestion (*1*) in opposition to the hydrogenolysis mechanism.

A simple kinetic model yields further in-

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* Under these conditions, the conversion is very selective for H_2S and C_4 products (butene-1, *cis*- and *trans*-butene-2, and *n*-butane). Butadiene and butyl mercaptan were not observed. Kinetically, the substantiated reaction scheme is

$$\text{Thiophene} \xrightarrow{k_1} \text{Butenes} \xrightarrow{k_2} n\text{-butane}.$$

sight. Assume that thiophene is desulfurized at a differential rate $k_S T$, i.e., first-order in fraction thiophene remaining, T, and that exchange is occurring at a rate which is first-order in displacement from equilibrium (*4*), i.e., $k_E(q_e - q_{\text{thio}})$ where q_{thio} is the atomic fraction of deuterium in thiophene. Finally, assume that for every differential conversion, $k_S T$, the H_2S deutero-isomers that are eliminated from the molecules are distributed binomially about the q_{thio}-value that obtains at that instant and are excluded from further exchange. The following rate equations then apply:

$$\frac{d(\mathrm{D_2S})}{d\tau} = [k_S T] q_{\text{thio}}^2,$$

$$\frac{d(\mathrm{HDS})}{d\tau} = [k_S T] 2q_{\text{thio}}(1 - q_{\text{thio}}),$$

$$\frac{d(\mathrm{H_2S})}{d\tau} = [k_S T](1 - q_{\text{thio}})^2.$$

The assumed first-order kinetics allow substitutions, $T = e^{-k_S\tau}$ and $q_{\text{thio}} = q_e(1 - e^{-k_E\tau})$, and a simplifying definition, $\rho = k_E/k_S$, can be inserted to produce the solutions:

$$\begin{aligned}
(\mathrm{D_2S}) &= q_e^2(1 - T) - \left(\frac{2q_e^2}{1+\rho}\right)(1 - T^{1+\rho}) \\
&\quad + \left(\frac{q_e^2}{1+2\rho}\right)(1 - T^{1+2\rho}), \\
(\mathrm{HDS}) &= 2q_e(1 - q_e)(1 - T) \\
&\quad - \left(\frac{2q_e(1 - 2q_e)}{1+\rho}\right)(1 - T^{1+\rho}) \\
&\quad - \left(\frac{2q_e^2}{1+2\rho}\right)(1 - T^{1+2\rho}), \qquad (1) \\
(\mathrm{H_2S}) &= (1 - q_e)^2(1 - T) \\
&\quad + \left(\frac{2q_e(1 - q_e)}{1+\rho}\right)(1 - T^{1+\rho}) \\
&\quad + \left(\frac{q_e^2}{1+2\rho}\right)(1 - T^{1+2\rho}).
\end{aligned}$$

These equations sum to the relation $(\mathrm{H_2S}) + (\mathrm{HDS}) + (\mathrm{D_2S}) = 1 - T$ which is the fractional molar conversion of thiophene and, furthermore, if $\rho = 0$, i.e., no exchange

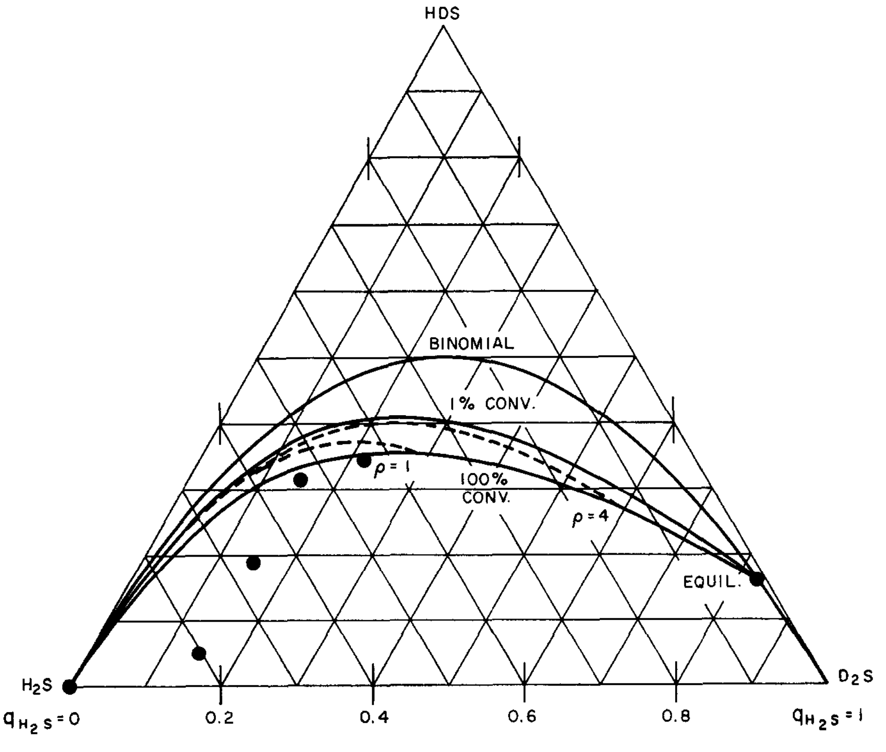

Fig. 1. Distributions of Hydrogen Sulfide Deutero-isomers.

reaction, the only product is hydrogen sulfide and $(H_2S) = 1 - T$.

The nature of these solutions is presented in Fig. 1 where the *normalized* concentrations of H_2S-isomers are plotted trilinearly. The binomial distribution $(0 \leq q_{H_2S} \leq 1)$ to be expected of a random exchange process is given by the upper curve. Distributions for conversions between 1 and 100% and for all values of ρ lie in the narrow band indicated which is depressed below the binomial curve. The nonbinomial character of the solutions is produced by the model assumption which removes H_2S-isomers from further exchange after their expulsion from thiophene. The illustrative reaction paths for two values of ρ show that at 100% conversion there exists an upper limit to the amount of deuterium to be observed in the H_2S-like molecules. This limit can be obtained from Eqs. (1) which can be used to show that

$$q_{H_2S} \equiv \frac{(HDS) + 2(D_2S)}{2(1 - T)} = q_e \left[1 - \left(\frac{1}{1+\rho}\right)\left(\frac{1 - T^{1+\rho}}{1 - T}\right)\right],$$

and, therefore, that

$$[q_{H_2S}]_{T=0} = q_e \left[\frac{\rho}{1+\rho}\right].$$

These two consequences of the model—a nonbinomial distribution and an upper limit to q_{H_2S}—would be critical objects of study in any further, more complete, work on this system.

The distributions we obtained in our experiments are shown by the data points of Fig. 1. The precision was low because the total H_2S-isomer concentration in the total product sample only lay between 2 and 4 mole%. However, the nonbinomial character is evident and the highest value of q_{H_2S} is 0.39 which is far displaced from the equilibrium value of 0.91†

Any support that these data and ideas have for Kolboe's suggestion merely makes a thorough investigation of this system, which we are engaged in, more desirable. We are also concerned with the role these reflections play in the conversion of benzothiophene and dibenzothiophene.

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† The assumption that H_2S-isomers undergo no further exchange leads to hydrogen and deuterium being eliminated from the "reaction system" and thereby changing the q_e as calculated from the reactant ratios. Under the present conditions, the extreme case of 100% conversion and *only* H_2S being formed would produce $q_e = 0.95$ instead of 0.91. This makes little change in the curves of Fig. 1. The hydrogen–deuterium balance necessary to correct this deviation was not deemed necessary in this work.