



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

ON THE MECHANISM OF BENZOTHIOPHENE HYDRODESULPHURIZATION

E. FURIMSKY

MAY 1978

For submission to Journal of Catalysis as a Research Note.

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 78-51

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

ON THE MECHANISM OF BENZOTHIOPHENE
HYDRODESULPHURIZATION

by

E. Furimsky

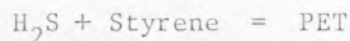
Energy Research Laboratories
Canada Centre for Mineral and Energy Technology
Department of Energy, Mines and Resources
Ottawa, Canada

Thiophenic ring containing species represent an important portion of sulphur compounds present in petroleum fractions. Therefore, benzothiophene (BT) is often used in model studies to explain the mechanism of hydrodesulphurization (HDS). The mechanism elucidation is based on the product distribution under variable temperatures, hydrogen concentrations, catalyst amounts, etc. Product evaluation is therefore an essential part of the work. Unfortunately, a number of products which one would expect to be formed are short-lived and as such cannot be detected.

The type and yield of products also depend on the experimental techniques applied. Thus, a static system, such as in autoclave experiments will result in different products than will the flow technique. This suggests that any mechanism proposed must be discussed in light of the experimental arrangements under which the results were obtained.

Recently, work on the mechanism of HDS of BT under different conditions has been published. The experiments have been performed using an autoclave (1) and using a flow technique in which pulses of BT were injected into the hydrogen stream at or near atmospheric pressure and then carried to the catalyst bed (2). Different routes are included in the proposed mechanisms as the result of different product distribution observed in these studies.

Daly (1), for example, observed the back reaction of H_2S with styrene leading to formation of phenylethanethiols (PET). Such reactions are possible in autoclaves because a high concentration of H_2S can be built up, thus shifting the equilibrium to the right.



There is, however, little chance for the back reaction to occur in the flow system because of the continuous supply of fresh hydrogen and removal of H_2S from the reactor.

The heteroring hydrogenation in BT occurs when a sufficient amount of hydrogen is present. Thus 2,3-dihydrobenzothiophene (DHBT) should be detected in studies conducted under high hydrogen pressure. At or near atmospheric pressure, the equilibrium between BT and DHBT is shifted to BT; therefore, DHBT may not be formed at all. This was confirmed by complete conversion of DHBT, at a low hydrogen pressure and a temperature of $400^\circ C$, over unsupported and supported molybdenum catalysts, either to BT or to styrene and ethylbenzene (2). Under these conditions quite extensive HDS of BT occurs, suggesting that the compound can be desulphurized without the heteroring saturation.

Two HDS routes, one with and one without preliminary heteroring hydrogenation, are generally accepted. The following simplified scheme for HDS of BT includes products which are usually detected, depending on the experimental arrangement; e.g., the products which originate directly from the reactant BT molecules:

INSERT SCHEME HERE

Here, 2-PET should be included in the event that the product is formed via ring opening in DHBT. Such an alternative can, however, be disputed on the basis of different bond strengths; e.g., the bond between sulphur and carbon is stronger if the carbon atom is aromatic, rather than aliphatic. In addition, the cleavage of the weaker bond leaves the SH group attached to the aromatic ring, in which case the C-S bond is about 15 kcal stronger than in aliphatic thiols (3). As the reactions always proceed in the direction of more stable products, the formation of 2-PET from DHBT is improbable. Other substituted thiophenols are often proposed in HDS mechanisms although they have not yet been detected. Using thermodynamic considerations, the stability of the intermediate phenols in the presence of hydrogen at approximately 300°C (Fig. 1) is comparable to that of styrene. Because of a lack of thermodynamic information, the comparison can be made only using thiophenol and styrene, assuming the same trend will persist for real species. Then, at about 300°C, the thiophenols may exist whenever styrene is detected. Increasing hydrogen pressure will have a more pronounced effect on the removal of styrene than of thiophenols as the change of mole numbers for the reactions indicates (Fig. 1). Failure to detect thiophenols simultaneously with styrene (2) suggests that the heteroring might be opened while avoiding the formation of these intermediates. It will be shown that such an alternative is theoretically possible.

The presence of an active catalyst is essential to achieve a high degree of HDS of BT. The very first step of HDS reaction, then, may involve intimate contact of the reactant molecule with the catalyst surface. Supported and unsupported molybdenum catalysts, most frequently used in HDS studies, are usually applied in a sulphided form. Anion vacancies adjacent to Mo ions are believed to be sites through which an interaction between the molecule and the surface, presumably via S heteroatoms, occurs. Such a model was postulated by Lipsch and Schuit (4) in their thiophene HDS study over supported molybdate catalysts. Although these authors assumed the catalyst to be in an oxide form, the model offers an alternative for speculations based on the presence of a sulphided surface. Under these conditions surface hydrogen is probably bound in SH groups. The hydrogen will be most likely present close to the C-S bond of BT molecule adsorbed at the anion vacancy. For sterical reasons the access of hydrogen is easier to the

C-S bond as depicted in Fig. 2. At this point a transition state between the surface and the reactant molecule, involving the SH hydrogen, may exist (bonds with broken lines in Fig. 2). Thus, the C-S bond can be broken as the result of the hydrogen migration. Using the bond strength arguments mentioned above, the hydrogen should migrate to the C of C-S bonds rather than S because the C-H bond formed here is much stronger than the S-H bond (5). This suggests that a styrene precursor is formed in which S may still remain in contact with the surface. Such an intermediate was proposed in the HDS of thiophene (6). The cleavage of the second C-S bond can proceed in a similar manner.

A sulphided surface is a necessary condition for the surface hydrogen to be present in SH groups. For an oxidic catalyst the hydrogen is believed to be in OH form (4). Because bond strength is about 25 kcal greater in O-H than in S-H (5), hydrogen transfer to the C-S bond is expected to be very slow for the oxidic surface. The higher activity of molybdate catalysts in sulphided form, generally observed, is in support of the arguments.

The proposed mechanism indicates that HDS of BT can be accomplished without the formation of thiophenol intermediates. Moreover, the surface vacancy can be filled with S without H_2S participation. It appears that the postulated transition state might also be applicable to BT molecules in case they undergo a flat adsorption.

Reference

1. Daly, F.P., J. Catal. 51, 221 (1978)
2. Furimsky, E., and C.H. Amberg,
Canad. J. Chem. 54, 1507 (1976)
3. Benson, S.W., Chem. Reviews 78(1),23(1978)
4. Lipsch, J.M.J.G., and G.C.A. Schuit, J. Catal. 15, 163(1969)
5. Sanderson, R.R., "Chemical Bonds and Bond Energy"
Academic Press, New York (1971)
6. Kolboe, S., and C.H. Amberg,
Canad. J. Chem. 44, 2623 (1966)

Captions to Figures

Fig. 1 Thermodynamic equilibrium of styrene and thiophenol in the presence of hydrogen.

Fig.2 Postulated transition state for HDS of BT

Scheme:

